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INTRODUCTION TO GENERAL CHEMISTRY

An Exposition of the Principles of
Modern Chemistry

BY

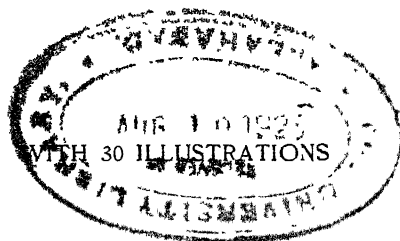
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TRANSLATOR'S NOTE

Professor Copaux's work presents in compact, yet clear form a large amount of information on the principles of chemistry as recognized today by the leaders in the science. I have endeavored to render the text into standard English, and thus make it available to a wider group of readers, to whom it will be a valuable guide.

Those who, like myself, began the study of chemistry just after the middle of the last century, will find many points of difference between this book and the manuals of the early days, yet the fundamental features of the science remain unchanged. The atom is still the unit of chemical action, and the balance is still, as in the laboratory of Lavoisier, the chemist's main reliance.

While the translation was in progress, Professor Copaux kindly sent a copy of the book with notes of corrections of a few typographic errors, and some changes in phraseology adding to the explicitness or comprehensiveness of the text. These suggestions have been given attention.

AUTHOR'S PREFACE

Van't Hoff once asserted at a conference, that he had not understood Avogadro's postulate until it became his duty to teach it. How many chemists and physicists have relinquished for all time the effort to comprehend certain physical principles that they are constantly applying, because they failed to understand them when first presented? Concerning these false starts, so difficult to correct, and which are due often to the unavoidable lack of precision in oral instruction and errors in note-taking by students, no book can assume to be so clear as to suppress them wholly, but an effort can be made to reduce them, and it is with this intention that this little book has been produced.

If it should aid students to form early in their studies correct notions of the fundamental principles of chemistry, and inspire confidence in the force of chemical theories, the author will feel that his object has been attained.

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CHAPTER I

THE CONCEPTION OF THE ELEMENT AND THE LAW OF CONSERVATION OF MATTER

The very diverse objects that surround us are associations of a small number of primary substances, called elements or simple bodies, the notions concerning which were not clearly formulated until the work of Robert Boyle, an English scientist of the 17th. century. He first set forth the theory that these simple substances are limited in number, but more than the four or five which had been generally assumed before his time. He further asserted that the properties of any compound depend on the proportions of its elements and their arrangements. This is the qualitative theory of combination as understood today. It was not proved at that time because chemists had not the means of isolating or distinctly indicating the actual elements. They knew how to prepare many compounds—reagents, acids, alkalies, salts, alcohol—but they knew little about the several gases and were quite ignorant of many of the elements.

About the middle of the 18th. century, the so-called "pneumatic chemistry" was actively devel-

oped during a score of years, by the discovery or identification of carbon dioxid, by Black, hydrogen, by Cavendish, chlorin, by Scheele, hydrogen chlorid and oxygen by Priestley, and thanks to the discovery of the last named, an explanation of the phenomena of combustion became possible. This explanation, the most important of all the phenomena of combination, was given by Lavoisier about 1775. All bodies that burn in air, *e.g.*, tin, zinc, mercury, take up oxygen, causing it to lose the gaseous form and form a metallic oxid. The substance of the metal is not lost, for from the accepted point of view, nothing is destroyed and nothing created; the increase in weight is due to the oxygen taken up. Lavoisier, who first conceived this view, gave a very striking demonstration of it in the case of mercury.

Mercury is gently heated for a long time in a sealed flask containing air. A red coating forms slowly upon the surface of the metal (the precipitate *per se*, of the older pharmacists), while at the same time the volume of the air diminishes. The two phenomena are interdependent, for the red deposit on being heated strongly, is reconverted into metallic mercury, with the emission of a gas that possesses the properties of oxygen as indicated by Priestley.

Reciprocally, the mercuric oxid in decomposing gives a weight of the metal as much less than that of the oxid as is equivalent to the weight of the oxygen evolved. The combination of carbon obeys

the same conditions, differing only from the metal in that the product is a gas, carbon dioxide.

Combustions being only instances of particular conditions of combination, a generalization can be made that "All combination of simple substances is made by the association of their masses, and this is expressed in Lavoisier's law: The mass of a compound is the sum of the mass of its constituents.

All the modern development of chemistry confirms this law of conservation of matter, which has never been found wanting even under most rigorous tests, one of the types of which is as follows:

Into two glass tubes, placed concentrically, are introduced respectively two solutions which are capable of reacting without marked violence. The outer tube is then sealed with a flame, and the apparatus carefully weighed. It is then inclined so as to bring the solutions together, and when the previous temperature has been attained it is again weighed. In operating thus with solutions of silver sulfate and ferrous sulfate, which liberate silver, or iodic and iodohydric acids, which liberate iodine, a loss of weight may be noted, ranging from 0.068 mg. to 0.199 mg. in the first case, and from 0.047 mg. to 0.177 mg. in the second. These differences are appreciable in careful and skillful work, but it has been discovered that they are due entirely to differences in the amount of moisture on the glass at the two periods. Under the influence of the slight heating, the glass loses some of the moisture on the outer surface, and this is taken up

again only very slowly. If this source of error is eliminated by a blank experiment, it will be found that the explanation is confirmed. (Landolt's experiments.)

Exchanges of Matter and Energy.—Thus the exactness of the law of conservation being greater than the exactness of our methods of measurement, it becomes us to admit it as dominant. Nevertheless, it is to a certain extent not absolute. Modern physics suggests that the mass of a substance may be a variable quantity according to the loss or gain of energy. A substance heated to 100° possesses more inertia, that is to say, more of mass, than when at zero, inversely, a system which disengages heat in its reaction will have lost by this some of the mass which it possesses before the given reaction. Otherwise expressed, matter and energy are interchangeable, in the same manner as the several forms of energy, such as electricity, heat, etc. are among themselves. What is conserved in a closed system without relation to the exterior, is the sum of the mass and the energy; of this sum the law of Lavoisier can be affirmed: "nothing is created; nothing is destroyed." The conservation of matter is a particular instance of a general law and involves the conservation of energy.

The law that rules the exchanges of energy and mass is such that an enormous variation of energy involves a very slight change of mass. Let D_m represent the variation of the mass of a substance, DE the corresponding variation of the total energy

of the same, V the velocity of light (say 3×10^{10} cm. per second, then

$$D_m = \frac{DE}{V^2}$$

In fact, even in energetic reactions, such as that between 16 gm. of oxygen and 2 gm. of hydrogen, producing 18 gm. of water, with a heat disengagement of 69,000 gram-calories, the weight lost is only

$$\frac{69,000 \times 4.18 \times 10^7 \text{ ergs}}{9 \times 10^{20}} = 3.2 \times 10^{-9} \text{ gm.}$$

that is, 0.00001 mg., a quantity out of the reach of our most accurate measuring instruments at this time. Whatever may be the ultimate application of these data, recently set forth, we can at present disregard them in the writing of equations and accept the law of Lavoisier as to the conservation of matter.¹

¹ Langevin. *L'inertie de l'énergie et ses conséquences* Conference à la Société française de Physique, mars, 1913.

CHAPTER II

THE LAWS OF CHEMICAL PROPORTIONS

The acceptance of Lavoisier's views marked the end of the purely qualitative phase of Chemistry; in less than a quarter of a century his work was completed by the elucidation of the quantitative laws, on the basis of which chemistry, at least, inorganic chemistry, has almost wholly rested for nearly one hundred years. These are: the laws of definite proportion by weight and volume and the law of multiple proportions.

Law of Definite Proportions by Weight (Proust's law).—*"In a given compound the proportion of the combined elements is a constant."* Thus, in analysing mercuric oxid the proportion of the metal to the oxygen will be always the same, provided the substance is pure. This condition is easy to realize in the case of mercuric oxid, but not for all compounds, and if there exists in the substance under analysis, impurities properly so-called, or accidental excess of any ingredient or an association of constituents different from the standard, such as peroxid or suboxid, the law of constant proportions is masked. It holds good, nevertheless, and the merit of Proust is that he demonstrated this fact in several cases of apparent abnormality, establishing the law of constant proportion, against the opposition of Berthollet (1805).

Law of Definite Proportion by Volume (Gay-Lussac's law).—*When two elements combine in the gaseous state, they do so not only in definite weight, but in definite and simple proportions by volume.* Further, if the product of the combination is a gas, its volume will bear a simple and definite ratio to the volumes of the constituents.

Gay-Lussac had his first suggestion of this law, in observing, in association with Humboldt, in 1805, that 100 volumes of oxygen unite with exactly 200 volumes of hydrogen in forming water. Three years later he extended his investigations to other gases and discovered that this simple volume relation is general.

Examples.—All the following gases measured under the same conditions of pressure and temperature give the results noted:

1 vol. of O and 2 vol. of H produce 2 vol. of water vapor.

1 vol. of Cl and 1 vol. of H produce 2 vol. of hydrogen chlorid.

2 vol. of N and 1 vol. of O produce 2 vol. of nitrous oxid.

1 vol. of N and 3 vol. of H produce 2 vol. of ammonia.

Moreover, the relation is shown in the case of the union of compound gases. Thus, 2 vol. of CO unite with 2 vol. of Cl to form 2 vol. of carbon oxychlorid (phosgene).

Law of Multiple Proportions (Dalton's law).—*When elements are capable of forming with each*

other more than one combination (a frequent case) *the weight of one element will bear to that of the other a simple multiple relation.* One of the best instances of this law is furnished by the series of nitrogen oxids. If we determine the composition of these, without discussing the method of analysis, and state the results directly in weights of the substance, the following figures will be obtained, all expressed in per cent.

	N	O
Nitrous oxid	63 6	36 4
Nitric oxid	46 6	53 4
Nitrous anhydrid	36 8	63 2
Nitrogen dioxid	30 4	69 6
Nitric anhydrid	25 9	74 1

No striking ratios are indicated by these figures, but if we restate them in terms of one of the constituents taken as 100, we get the following:

	N	O	ratios
Nitrous oxid	100	53 14	1
Nitric oxid	100	106 28	2
Nitrous anhydrid	100	159 42	3
Nitrogen dioxid	100	212 56	4
Nitric anhydrid	100	265 70	5

Thus, by an easy change a relation previously concealed is unmasked, a result by no means infrequent in physical science. Sometimes the progression of ratios is less regular, for instance, the two phosphorus chlorids show a relation of 3 and 5 respectively. In general, combinations between any two elements are likely to follow the natural order of whole numbers both in volume and weight relations.

CHAPTER III

ATOMIC THEORY

Dalton's Hypothesis.—The laws of chemical proportion have been systematized by the theory of the atomic structure of matter, a very ancient one, the first ideas of which were based on the following reasoning. Every mass is divisible, and the divisibility is well beyond the limits of our finest instruments. Does it then follow that such divisibility is infinite and may go on until the mass is annihilated? No, for it is not allowable to assume that a material object should be made up of particles without mass or dimensions. It is necessary, therefore, to assume a limit to the divisibility. This limit is the *atom*, an indivisible particle.

The atomic theory remained for centuries merely a philosophic conception, with no other demonstration except that just noted, but sustained by a sort of intuition of its truth, until in 1808, Dalton gave it a positive and fruitful form, in setting forth that each element is made up of characteristic atoms, possessing a definite and invariable mass. According to this view it is logical to assume that when atoms enter into combination, they preserve their masses, obeying Lavoisier's law, and form by juxtaposition a new system which is termed a

molecule, to distinguish from the isolated atom. Further, the masses of atoms cannot be divided or destroyed; their combinations can only be made by distinct and definite quantities, a fact which accords with Proust's law. Finally, if two different kinds of atoms form several combinations, the ratios will be graduated by equal atomic masses progressively, that is, obey the law of multiple proportions. Thanks to the conception of the atom, another law, laboriously developed by the analytic researches of the 18th. century, becomes directly comprehensible; this is the law of the equivalences of the elements. Certain elements can mutually replace each other in combination, acting as chemical equivalents, the replacement occurring in ratios specific for each element, as determined by experiment. Now, under the atomic theory this fact is easily explained. The specific ratios are those of the respective atomic weights, and, consequently, the same relations should obtain in the substitutions as in combination.

Example.—Methane, CH_4 , reacts with chlorine to form a series of chlorinated derivatives, of which the composition by weight to a constant weight of carbon is shown in the annexed table.

	Carbon	Hydrogen	Chlorine
Methane.....	100	33.3	
Chlormethane.....	100	25.0	295
Dichlormethane	100	16.6	591
Trichlormethane... ..	100	8.3	887
Tetrachlormethane....	100	1183
(Carbon tetrachlorid)			

The decrease of the hydrogen and its replacement by chlorin follows a definite arithmetic progression of which the ratio is 295 of chlorin to 8.3 of hydrogen, therefore, the quantities of 295 and 8.3 respectively, or more simply 35.5 and 1, are the equivalents of the two elements. It is said, therefore, that one atom of chlorin displaces one atom of hydrogen, inasmuch as the weight of 1 atom of chlorin is 35.5 times that of hydrogen. If, now, we determine the composition by weight of hydrogen chlorid it will be found that there is a proportion of 35.5 parts of chlorin and 1 part of hydrogen, and this justifies the assumption that the molecule of hydrogen chlorid is made up of 1 atom of each of the elements, an assumption which is confirmed by other data.

DETERMINATION OF ATOMIC WEIGHTS

Primary Approximation

By collecting data from a number of such cases as discussed in the last section, and basing the calculations on the weight of the hydrogen atom (so far as known the lightest of all) a table of coefficients or relative (atomic) weights of the elements can be arranged, a table of great usefulness in chemical procedures, since it shows clearly the proportions in which the elements combine or replace each other. Such a table will be, however, somewhat arbitrary in the calculation of atomic weights upon the sole basis of the reasoning just presented. Thus, water being composed of 8 parts

by weight of oxygen and 1 part by weight of hydrogen, the atomic weight assigned to the former element will depend not only on these proportional numbers, but also on the constitution that we assign to the molecule of water. If this molecule is composed of one atom of each element, then the atomic weight of oxygen (relative to hydrogen as unity) will be 8, but if this view is too simple, that is, for example, if the water molecule is composed of 2 atoms of hydrogen and 1 of oxygen, then the atomic weight of the latter element must be 16 in order to satisfy the conditions determined by experiment.

Avogadro's Theory and the Molecular Weights of Gases.—The uncertainties noted in the preceding paragraph are eliminated, at least for gaseous elements, by the very important suggestion offered in 1811, by an Italian scientist, Avogadro, as follows:

All gases taken at the same conditions of temperature and pressure contain in equal volumes equal numbers of molecules. This statement, demonstrated only by actual results, rests on the following observation, the simplicity of which is out of proportion to the importance of the applications. Gases are eminently compressible and dilatable; it may be inferred, therefore, that their molecules are separated by great spaces, which spaces are increased or diminished in any change of the volume of the gas. Now all gases have sensibly the same coefficient of compression (law of Boyle and Mariotte), and the same coefficient of expansion (law of Gay Lussac).

Reacting in the same manner towards equal variations of temperature and pressure, they should be constituted in the same manner, that is, by material centers equally spaced on the average, equal numbers of these in equal volumes.

Let n be the number of molecules in a given unit of volume, w and w^1 the weights of molecules of the two gases, of which the respective densities are d and d^1 . The relation of the densities being, according to definition, equal to the relative weights of equal volumes of the two gases, we have

$$(1) \quad \frac{d}{d^1} = \frac{nw}{nw^1} = \frac{w}{w^1}$$

It is true that the absolute values of w and w^1 are unknown, but taking one of them as unity, say $w = 1$, then the relative weight of one gas will be deduced by the formula

$$w = \frac{d}{d^1}$$

For example: The molecular weight of chlorine relative to that of hydrogen is in proportion to their respective densities,

$$\frac{2.491}{0.0695} = 35.8$$

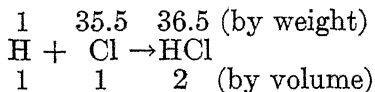
a number close to 35.5 obtained by other methods.

The agreement is not perfect because the postulate of Avogadro is exact only as far as the approximations of the laws of Boyle and Mariotte, and of Gay Lussac, but the closer a gas is brought to a

perfect condition the closer is its conformity to the principle.

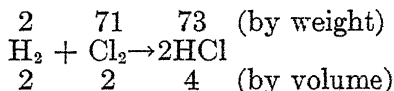
Atoms and Molecules.—The application of the above principle is as valid for compound as for elementary gases, inasmuch as the physical properties are identical; nevertheless the rule meets some exceptions, unless we distinguish the atom from the molecule more exactly than has been so far here pointed out. For instance, hydrogen chlorid has a density of 1.268; its molecular weight according to the Avogadro postulate should be $1.268 \div 0.0695 = 18.25$, but the previous calculation gives us 36.5. To eliminate this difficulty, it is only necessary to adapt the Avogadro postulate to the data derived from the study of the volumes of gases entering into combination.

We know, for instance, that two volumes of hydrogen chlorid are formed by the union of one volume of hydrogen and one of chlorin. Representing the two elements by their symbols (which also represent the respective weights and volumes of their atoms) we will have

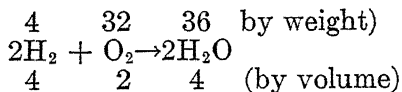


This presentation will not be in accord with the Avogadro principle, which requires that the compound (HCl) should occupy the same volume as the constituent gases H and Cl. If, however, we assume that the two gases in the free state consist of molecules each containing two atoms, the mole-

cules of both simple and compound gases will occupy the same volume and the statement will become



Under this view, known to Avogadro, but later independently pointed out by Ampère, and confirmed by all subsequent investigations, the given reaction is seen to conform at once to the results of experiment and the requirements of theory. The same observation may be made in connection with the synthesis of water. The only equation that will correctly express at once the data by both weight and volume, is



All of the molecules (H_2 , O_2 , H_2O) occupy the same volume. From these considerations the following definitions are derived:

The *atom* is the smallest mass of any element capable of entering into combination, such as H and Cl in HCl.

The *molecule* is the smallest amount of any substance, element or compound, capable of existing in the free state, such as H_2 , O_2 , Cl_2 , HCl, H_2O .

Lastly, since hydrogen serves as the unit of molecular weight, the molecule of hydrogen becomes equal to 2 and the expression (1) (p. 13)

correctly applied gives definitely the molecular weight of any gaseous substance.

$$\frac{w}{2} = \frac{d}{0.0695}, w = \frac{2}{0.0695} \times d = 28.8 \times d.$$

Examples.

	Density compared to air	Molecular weight $28.8 \times d$	Formula
Hydrogen chlorid	1 268	36 5	HCl
Chlorin .	2 491	71 6	Cl ₂
Water (vapor).	0 623	17 8	H ₂ O
Oxygen	1 1053	31 8	O ₂
Ammonia .	0 596	17 1	NH ₃
Nitrogen	0 967	27 8	N ₂

It must be borne in mind that while the density of any substance in the state of gas fixes its molecular weight, it may not determine its representative formula, which latter must be based on other data as well, especially on reactions in which the atoms take part as such. Thus, arsenous chlorid has a density of 6.3 and a molecular weight of 181.2. These data do not suffice to establish a formula, but quantitative analysis shows that the compound contains in 100 parts, by weight, 41.3 of arsenic and 58.7 of chlorin, therefore 106.3 grm. of the latter element in 1 gram-molecule of the compound (181.2). The atomic weight of chlorin being 35.5, there are evidently 3 atoms of chlorin in the

molecule ($106.3 \div 35.5 =$ nearly 3), with 1 or more atoms of arsenic. The formula is, therefore, not yet definitely fixed, but the possible forms are much limited. The simplest is AsCl_3 , which corresponds to $\text{As} = 74.9(181.2 - 106.3)$, a figure confirmed by other methods which will be discussed later.

When a formula is established it indicates not only the proportions by weight of the elements present, but if these are gases, the volumes in which they are united to form two volumes of the compound in the gaseous state. This unification of formula is one of the fortunate results of the Avogadro postulate.

Monatomic and Polyatomic Molecules.—The several non-metals which have been under discussion have all diatomic molecules, that is, H_2 , O_2 , Cl_2 , N_2 , but this is not universal among the known elements. Phosphorus in the gaseous condition has a density of about 4.4 at 500° , which indicates a molecular weight of 126. On the other hand, hydrogen phosphid has a density of 1.184, and, therefore, a molecular weight of 34. In view of the low atomic weight of hydrogen, it is evident that the atomic weight of phosphorus cannot differ much from 30; the obvious explanation is that in the conditions of the experiment, namely, phosphorus vapor at 500° , the molecule contains 4 atoms, indicated by P_4 , and it is termed *tetrameric*. Arsenic exhibits the same abnormality. On the contrary, mercury has a density of 6.97, with a molecular

weight of 200, but mercuric chlorid in gaseous condition has a density of 9.8 and a molecular weight of 271. Several characteristics in the reactions of mercuric chlorid show that its formula is HgCl_2 , from which it follows that the atomic weight of mercury is 200 ($271-71$) the same as its molecular weight. The molecule of mercury in the state of gas consists of a single atom and is termed *monatomic*. This abnormality is not infrequent among the so-called metallic elements.

Atomic Weights of Solid Elements

This phrase will serve to distinguish those elements which have such high boiling points as make great difficulty in measuring their densities in the state of gas. For these the law of Avogadro obviously has no satisfactory application, but other principles have been found applicable, among which is the law of atomic heats, announced first in 1819, by Dulong and Petit, and stated in the following form:

The atomic heat of an element is the product of its specific heat by its atomic weight, and is in most cases a close approximation to the number 6.4.

That is to say, the atoms of all elements in the solid state have nearly the same capacity for heat. The annexed table¹ presents some of results of investigations along these lines.

¹ The data for this table are taken from a paper by Richards and Jackson, *Zeitschr. physik. Chem.*, 1910, **70**, 414. The order in which the elements are here arranged is not that of either R. & J's. paper or the French text. I have also added from the original paper, the fifth column—Tr.

Element	Atomic weight (1909)	Specific heat -188° to $+20^{\circ}$ in calorie units	Atomic heat in calorie units -188° to $+20^{\circ}$	Atomic heat in calorie units $+20^{\circ}$ to $+100^{\circ}$
Al	27 1	0 1748	4 73	5 8
Fe	55.85	0 085	4 78	6.5
Mn...	54 93	0 0931	5.12	6.7
Cr	52 1	0 0794	4 14	5 6
Ni	58.68	0 0870	5 10	6 3
Co...	58 97	0 0828	4 88	6.2
P....	31 0	0.169	5 24	6 3
As	75 0	0 0705	5 29	6 2
Sb..	120 1	0 0469	5 62	6 0
Bi...	208 0	0 0284	5 91	6 3
C (Graphite) ..	12 0	0 0959	1 15	2.4
Si..	28.3	0 118	3 34	5 2
Ag..... . . .	107.88	0 0511	5 51	6 1
Cu.	63 57	0 0789	5.01	5.9
Mg	24 32	0 208	5 06	6 0
Zn	65 37	0 0846	5 53	6.1
Cd.	112.4	0 0515	5 79	6 2
Sn.	119.0	0 0502	5.97	6 5
Pt.	195.0	0 0279	5 45	6 3
Pd..	106 7	0 0517	5 51	6.3
Pb	207 1	0.0300	6.21	6 3
Tl	204 0	0 0296	6.04	6.7
Au	197.2	0.0297	5 86	6 1
Mo	96 0	0 0555	5 33	5 7
S....	32 07	0.131	4.20	5.6

Inspection of the table will show that while it will be unsafe with the data at hand to use 6.4 as a controlling figure for atomic weights, nevertheless the postulate of Dulong and Petit has been of much service in checking up other determination of these weights. For example, the percentage composition of silver chlorid indicates that the atom of silver has a relative weight of 107.88, but this calculation depends entirely upon the assumption that the chlorid is AgCl , which has been accepted, but such assumption receives additional support when we note that the atomic heat approximates the figure indicated by the postulate of Dulong and Petit.

The table also shows that two elements that are universally recognized as closely related chemically, namely, carbon and silicon, have specific heats which agree neither with the general rule nor with each other, but it would be the same with other elements if the measurements were made at lower temperatures. In fact, Nernst has shown that the specific (or atomic) heats tend to diminish as the temperature approaches the absolute zero, while the values seem to advance and approach more close to 6.4 as temperature increases. Carbon approaches the normal figure when the determination is made at 600° , the data being $12 \times 0.441 = 5.29$.

The postulate of Dulong and Petit is therefore a limited one, which is in many cases sufficiently accurate at ordinary temperatures to be of not

infrequent applicability. A more definite expression of it, as a result of researches now in course, will doubtless give important information concerning the physics of the elements.

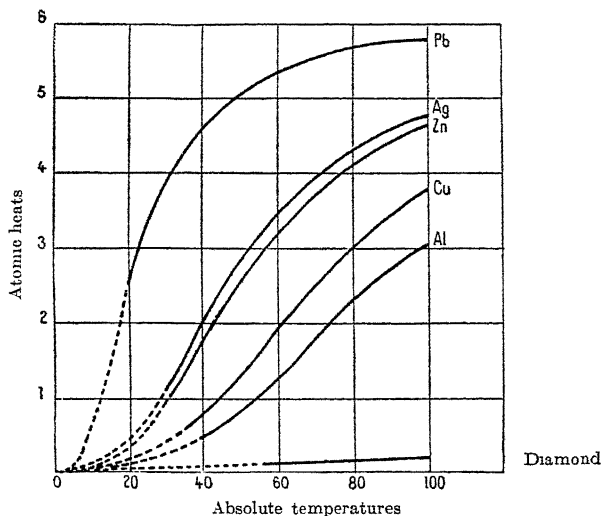


FIG. 1.

Isomorphism (Mitscherlich's law).—In the same year, 1819, in which Dulong and Petit announced the law just discussed, E. Mitscherlich proposed another method for checking up the atomic weights of the elements not easily volatilized, or what amounts to the same thing, determining the formula of a compound (see Appendix A). The method is based on the resemblances in crystalline forms. Before Mitscherlich's publication, de Lisle, Leblanc and Vauquelin had remarked that ammonium

can replace potassium in alum without affecting the form of the crystal, and that a crystal of ferrous sulfate will grow regularly in a solution of copper sulfate. Such observations, supplemented by many others, were collated by Mitscherlich and the principle involved formulated as follows:

When two substances have the same crystalline form and are found to be capable of crystallizing together in all proportions, the molecules have the same form and the compounds should be represented by formula of the same type. Such substances are called isomorphous.

For instance, ammonium hydrogen phosphate and ammonium hydrogen arsenate are isomorphous, that is, the crystals of each have the same form, the same symmetry, and the same angles and should, therefore, be represented by corresponding formulas, to wit:



Similarly, the hydrated sulfates of the so-called "magnesian" series, containing Mg, Mn, Fe, Ni, Co, have a common form and are all represented by a formula of the type $\text{MSO}_4 + 7\text{H}_2\text{O}$, in which M stands for any one of the metals. The atomic weights of H, S and O being known, that of the metal present is easily determined by a simple analysis of the sulfate.

The application of the principle of isomorphism is only comparative, but the instances are so numerous among salts that there are very few

elements to which the principle is not applicable with advantage. An instance is found with silicon. This element is very difficult to volatilize and has an abnormal specific heat, so that neither the method of vapor density nor that of Dulong and Petit can be employed to determine its atomic weight. It forms a volatile chlorid, the molecular weight of which, determined by the vapor density is 171, but this datum alone cannot fix the formula. It was for a long time thought that the molecule is Si_2Cl_4 , which will give 14.1 for the atomic weight of silicon, and lead to the formula SiO for silica, but Marignac recognized the isomorphism of strontium and zinc fluosilicates and fluostannates. The atomic weight of tin being known, although only by the method of specific heat, it could be shown that the fluostannates have the formulas, respectively,



and the fluosilicates



Under this formulation, the atomic weight of silicon becomes 28.3, and the formula of silica SiO_2 , which conforms to all previously known facts, and has not been put in doubt by any subsequent investigation.

It is true that in general isomorphism is not as precise as the law of Mitscherlich indicates. The angles of isomorphous salts are rarely exactly

equal, often showing a difference of several degrees. Simultaneous crystallizations are usually possible only within limits, not in all proportions. Moreover, many substances are known which, though isomorphous, do not have the same type of formulas. Instances of this kind are found among the complex tungstates, but these compounds are of high molecular complexity and have some close resemblances, so that isomorphism stands as index of analogy in composition, even in the unusual cases in which it does not accompany complete agreement in type of formula.

Determination of Atomic Weights by Transparency to x-rays. Benoist's method (1891).—The atomic weight of a given element has a specific relation to the power of the element to transmit the *x-ray*. If a photographic plate is enclosed in black paper, and upon this are placed different elements in the form of prisms cut to the same shape and dimensions, and a beam of *x-rays* allowed to fall uniformly upon these masses, the impression upon the sensitive plate will, of course, be in proportion to the power of the given substance to transmit the ray. If, now, we take some element, say aluminum, as a standard, and modify the thickness of the other prisms until the effects of the rays are equalized, it will be found that the relative thicknesses are in inverse proportions to the atomic weights, that is, the thicknesses will be greater the smaller the atomic weight, the relations being capable of being expressed by a continuous curve, which permits

the empirical deduction of the atomic weight of any element by its equivalent transparency to the x-ray. One advantage of the method is independ-

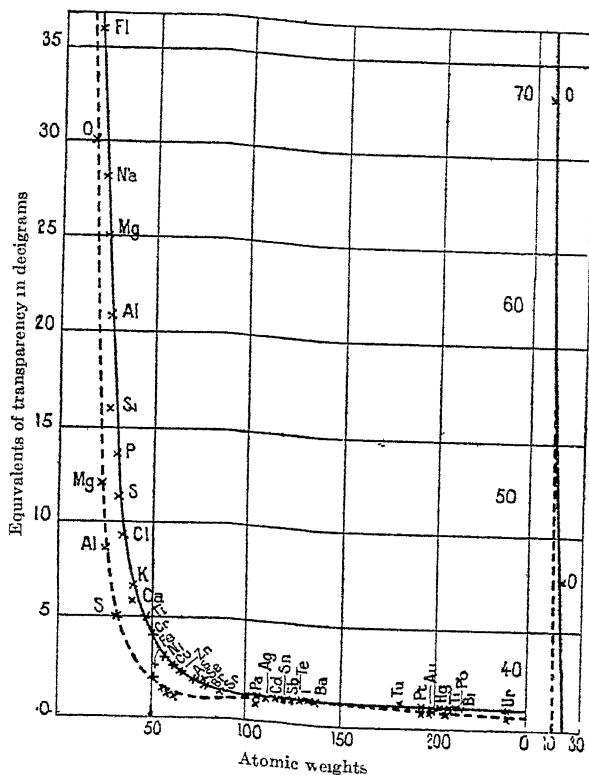


FIG 2 —The two curves, respectively continuous and broken, represent x-rays of different wave-lengths.

ence of the physical state, whether solid, liquid or gaseous. It is also applicable to compounds, because the molecular opacity of a substance is the

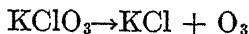
sum of the molecular opacities of its elements, thus permitting the determination of the equivalent transparency and the atomic weight of an element not yet isolated. It is a universal method but precise only in the case of elements of low atomic weight as the diagram (Fig. 2) shows by the form of the curve.

An Example of the Precise Determination of an Atomic Weight

A. *By Analysis*.—The methods enumerated so far have had for their object rather the fixing of the relative magnitudes of the atomic weights than the exact figures. To obtain the figures given in the table published each year under international agreement, a number of procedures must be followed, which are in the nature of successive approximations.

Take as an example the case of chlorin. In a preliminary series of determinations, the approximate atomic weight of it has been ascertained, and also the probable formulas of its compounds, by the analysis of hydrogen chlorid, the determination of its vapor density and that of chlorin itself. Hydrogen chlorid is a gas not easily handled, highly hygroscopic, and not suitable for very exact analysis. Berzelius, later Marignac, and still later Stas, chose other chlorids, more stable and capable of being weighed with greater accuracy, which conditions compensated for the fact they were obliged to adopt indirect methods, such as the following:

1. Decomposing potassium chlorate by heat into potassium chlorid and oxygen



The weight of the oxygen being ascertained, the molecular weight of the potassium chlorid can be calculated.

2. Transforming a known weight of potassium chlorid into silver chlorid, from which the molecular weight of the latter salt can be determined.

3. Transforming a known weight of silver into silver chlorid, from which can be deduced the atomic weight of the metal and then of chlorin and potassium.

First Operation.—64.690 gm. of potassium chlorate after heating left a residue of 39.357 gm. of potassium chlorid, and evolved 25.333 gm. of oxygen. The atomic weight of oxygen being taken at 16, the equation, based on the reaction as given above is

$$\frac{\text{KCl}}{3 \times 16} = \frac{39.357}{25.333} \quad \text{KCl} = 74.57$$

Second Operation.—17.034 gm. of potassium chlorid are dissolved in water, a little nitric acid added and then solution of silver nitrate. Silver chlorid is precipitated, which is collected, washed and dried. The weight will be found to be 32.749 gm.

$$\frac{\text{AgCl}}{74.57} = \frac{32.749}{17.034} \quad \text{AgCl} = 143.37$$

Third Operation.—16.469 gm. of silver are dissolved in dilute nitric acid and precipitated with sodium chlorid. The silver chlorid obtained weighs 21.860 gm.

$$\frac{\text{Ag}}{143.37} = \frac{16.469}{21.860} \quad \text{Ag} = 108.01$$

This number deducted from the molecular weight of silver chlorid gives 35.36 for the atomic weight of chlorin, and 39.21 for that of potassium. Eliminating sources of error by improvement of apparatus and manipulation and reducing all weights to weights in vacuum, the accuracy of the determinations may be materially increased, and the numbers at present accepted, as the result of such improvements are correct to about the second decimal place.

$$\text{Cl} = 35.46 \quad \text{Ag} = 107.88 \quad \text{K} = 39.10$$

B. *By Synthesis*.—Owing to the progress in methods of physical measurement, the synthesis of hydrogen chlorid has been lately used to determine its composition with as much accuracy as in the analytic method. The procedure was carried out by Dixon and Edgar in 1905. The chlorin, prepared by electrolysis of fused silver chlorid, was liquefied, sealed in a tube and weighed. The hydrogen was prepared by electrolysis of barium hydroxid solution, dried and absorbed by palladium, its amount ascertained by the increase of weight of the metal. Then, in an apparatus, specially designed, the hydrogen, set free by heating the palladium, was brought in contact with the chlorin, with which it combines actively forming hydrogen chlorid which was condensed by ice-cold water introduced into the apparatus. The slight excess of chlorin (which was maintained in the experiment in order to assure the complete combination of the hydrogen) was determined by displacement of iodine from an

iodid. The weights of the chlorin and hydrogen combining being known, that of the uncombined chlorin having been deducted the calculation of results gave $\text{Cl} = 35.46$, referred to $\text{O} = 16$.

Remarks.—The atomic weights that have been used in these calculations as well as those given in the tables published under international agreement, are based on $\text{O} = 16$, and not on $\text{H} = 1$. This is done to avoid frequent modifications, as the combinations of oxygen with the several elements are more numerous and more stable than those of hydrogen, the latter, indeed, are rarely used in the determination of atomic weights. Whenever the atomic weight of oxygen is modified to accord with more exact determinations of its relation to hydrogen, it would be necessary to make numerous changes in the atomic weights of those elements which rest on the comparison with hydrogen. It has been considered more advantageous to fix the atomic weight of oxygen at 16, which gives for hydrogen 1.008, a figure not appreciably different from unity.

RECENT DEVELOPMENTS OF THE ATOMIC THEORY

The atomic theory has recently found further justification in certain physical investigations, and especially in the determination of Avogadro's constant. This is a number, designated by N , representing the actual number of molecules contained in the unit volume of a gas. The relative atomic weights are an abstract statement of the fact. The unit volume is by agreement fixed as the volume

occupied at 0° and 760 mm. by a gram-molecule of any gas. Taking hydrogen as an example

$$\frac{2}{0.0695 \times 1.293} = 22.3 \text{ liters (22,300 c.c.)}$$

Several methods may be employed to obtain the constant, the results of which differ by a maximum of 20 per cent., which is a fair approximation considering the difficulties of the problem.

One of these procedures is founded on the property that matter in the fluid state has its molecules in constant and confused motion. In the state of gas, the molecules are constantly striking each other and the walls of the containing vessel, and rebounding, the motion being very rapid. The rate and extent differ with different gases (1700 meters per second in hydrogen at 0°C.; 425 meters per second in oxygen at the same temperature). The activity increases with temperature increase, and ceases entirely at the absolute zero. In liquids, which are less mobile, the speed is much diminished, but not entirely suppressed. It is distinctly perceptible by introducing into any liquid a very fine powder of some material not readily soluble, and examining a drop of the mixture under the microscope. The particles of the powder will be found to continue indefinitely in constant motion. This motion (called the brownian movement) is due to the imparting of the molecular motion of the liquid to the suspended material, and is irregular and variable. From the suggested

explanation, a basis of calculation has been secured which gives for the Avogadro constant, the value of 7×10^{23} , that is, this number of molecules is contained in the unit volume of gas (22.300 c.c.) at 0°C . and 760 mm. Otherwise stated, if each molecule was enlarged to the size of a common grain of sand, say 1 cu. millimeter, the volume of the gas containing such enlarged molecules would be increased in the same scale and a portion thereof that occupied 1 cu. millimeter at the standard temperature and pressure would occupy the space of a prism 1 sq. kilometer on the base and 31 meters high. The Avogadro constant also fixes the absolute weight, in decimals of a gram, of a hydrogen molecule as

$$\frac{2.016}{N} = 2.86 \times 10^{-24}$$

and that of the atom of hydrogen as

$$1.43 \times 10^{-24}$$

CHAPTER IV

GENERAL CHARACTERS AND INTERRELATIONS OF THE ELEMENTS

Several hundred thousand compounds are known, derived from a limited number of elements. The list at present includes a little over four score, and is slowly increasing by the discovery of new ones. It is evident that these substances are not likely to lack resemblances, in fact, some of them can be readily grouped into natural families, and yet such marked differences exist between many that, in inorganic chemistry, they are of necessity described in separate sections. It is, therefore, one of the most important points in the progress of chemistry to discover the relations between the elements, and to ascertain how far the attractive supposition of the fundamental unity of matter is justified.

Prout's Hypothesis.—The simplest view is to consider the elements as condensations of hydrogen atoms, which is the lightest of all. When this view was suggested in 1815 by Prout, an English physician and chemist, it seemed justified by the fact that the accepted atomic weights were mostly whole numbers, that is, simple multiples of the

atomic weight of hydrogen. It being shown later that many of these weights are not whole numbers, Prout's view fell into disrepute, but not without having done service in stimulating investigation by Dumas, Marignac and Stas to determine more precisely these weights. A recent observation by Langevin has given new interest to Prout's view. This is, that while the atomic weights of most of the elements are not whole numbers, many of them depart but little from such form, especially in the case of the low atomic weights. Thus, taking hydrogen as unity the following figures will be obtained.

He	3 96	Li	6 88	Cl	9.02	B	10 91
C	11 90	N	13.89	O	15.87	F	18 84
Na	23 81	Mg	24 12	Al	26 88	Si	28 07

May not these small departures from the nearest whole number be due to a slight loss or gain of matter, correlated with an enormous variation of energy, according to the principles already set forth concerning the equivalence of matter and energy (p. 5)? The atoms of the primordial substance—hydrogen, or perhaps helium—may have gained or lost by their union a mass equal to the quotient of the variation of energy by the square of the velocity of light, and as the departures from whole numbers correspond to a considerable variation of energy, according to the formula given on p. 5, it will be easy to understand the extreme stability of the new substances produced by the condensation

of the atoms of the primordial matter, and the difficulty so far encountered in converting one element into another.

Classification.—A chemical classification is the first step to a recognition of affiliations, otherwise obscure, between the elements. At first sight we can recognize two important groups; the alkali-metals and the halogens. The alkali-metals, Na, K, Rb, Cs, especially the last three, have many resemblances. They have the same general appearance, decompose water actively, disengaging hydrogen and forming energetic bases. Their compounds have formulas of the same type, *e.g.*, KCl, NaCl, Na_2SO_4 , K_2SO_4 , and some of their properties are so similar that the analytic separation of them is difficult.

The three halogens, Cl, Br, I, are all colored, all possess a strong, offensive odor, their physical constants, such as volatility, solubility, etc. are in the main progressive in the order of their atomic weights. Their compounds with hydrogen are all strong acids, the salts of which are isomorphous.

Between these two groups, well characterized and exactly opposite in their chemical properties, are many elements much less easy to group, or of which the relationships are not at all close. A full classification was not approached until 1863, when Mendeleeff published the suggestion of his "periodic system," founded on the following principle: If we set down the elements in the order of their known atomic weights, we will find that after each series

of seven or eight items, an element will be found that bears a strong resemblance in general properties to the seventh or eighth antecedent. This result is expressed in the approximate law, diagrammatically shown in Fig. 3, by the statement that

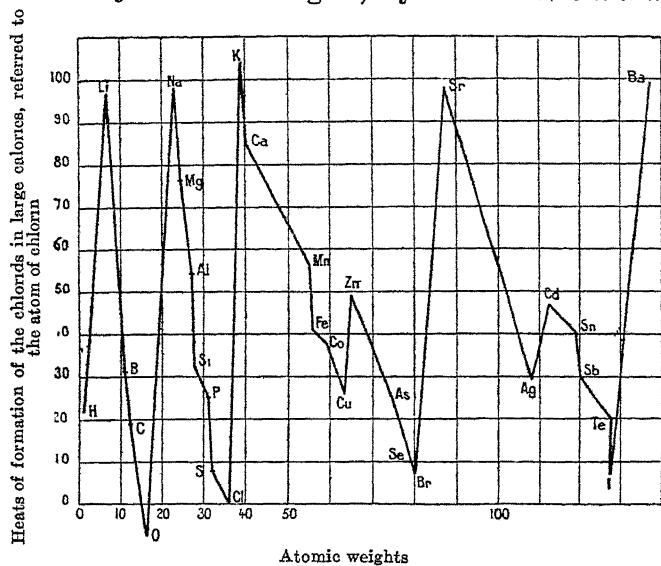


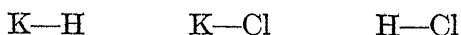
FIG. 3.

the physical and chemical properties of the elements are periodic functions of their atomic weights. Similar suggestions had been made before Mendeleeff, with somewhat less precision and in slightly different form, by Newlands in England and Béguyer de Chancourtois in France. The latter constructed a model in which the elements were inscribed on a helix wound upon a cylinder, the

generatrices indicating the natural families. This model is still in the collection of the École de Mines, and was called the "telluric screw."¹

The new feature of the Mendeleeff system is that it takes as the criterion of chemical analogy not a collection of miscellaneous properties, but a character, specific and universal, the valency of the element.

Valency.—The valency of an element is the number of atoms of another element with which one atom of the given element can combine. Thus, potassium forms a hydrid, KH, a chlorid, KCl, and chlorin forms a compound with hydrogen, HCl. One atom of each element saturates an atom of the other, or, taking hydrogen as a standard, we can say that potassium and chlorin are monovalent, that they have exchanged, or fixed, their respective valencies, and the relations can be expressed by the formulas:



With oxygen, potassium forms an oxid, K₂O, hydrogen forms the oxid H₂O; therefore, oxygen is bivalent, thus,

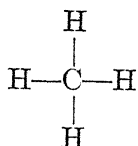


¹ An early suggestion, perhaps the earliest, of significant numerical relations between the atomic weights was made by Dobereiner in 1816. Carey Lea, a Philadelphian, made an extensive comparison, several years before Newlands' work. See *Amer. Jour. Sci.* [2], 1860, 29, 98, and some subsequent issues.—Tr.

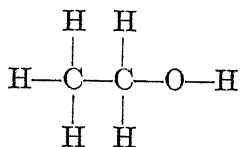
Nitrogen is trivalent, as determined by the formula for ammonia,



and carbon tetravalent as indicated in the formula of methane.

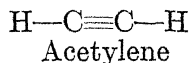
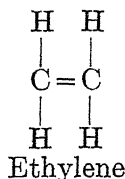


Arranging the elements in any compound in such manner that the respective valencies are satisfied, gives what is called a *structural* or *graphic* formula, of which many thousands have already been obtained, at least in organic chemistry, this result being largely due to the almost invariable tetravalence of carbon. Ethyl alcohol will serve as a simple example of the application of the principle, its structural formula being,

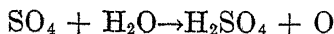


This formula implies that carbon can combine with itself, in this case by a single valency of each atom, but it is accepted that such union may be by

several valencies, giving rise to a class of compounds termed *unsaturated*, such as,



Electrochemical Measurement of Valency (Faraday's Laws).—This method, less widely applicable, but very exact, is based upon the laws of electrolysis discovered by Faraday. When a substance is capable of decomposition by the electric current (which is generally the case with acids, bases and salts in solution or in the melted state), the metal is deposited at the negative pole (cathode) and the non-metal at the positive pole (anode). Copper chlorid, for example, is decomposed into copper, which is deposited as a coating on the negative pole, and chlorin which escapes at the positive pole. If a sulfate is used, say, copper sulfate, CuSO_4 , the products are the metal and the acid radicle, SO_4 . The latter being unstable in the free state, reacts with the solution-water producing sulfuric acid and oxygen,



A salt of an alkali-metal and a bibasic acid, as Na_2SO_4 , is decomposed into Na_2 and SO_4 , both of which react with the solution-water and give rise to 2NaHO at the cathode, and H_2SO_4 at the anode. Whatever may be the substances resulting from

these secondary reactions, the amount of the original substance decomposed is dependent strictly on the amount of current passing through the solution, a principle which is expressed in two rigorous laws, as follows:

With a given compound, the amount of substance set free at each electrode is proportional to the quantity of current which is traversing the solution. With different compounds, the same amount of current will set free quantities that are chemically equivalent.

Take, for example, a solution of silver nitrate, AgNO_3 , undergoing electrolysis; the silver deposited at the cathode is strictly proportionate to the current supplied, and for a current equal to 96494 coulombs, there is deposited a gram-atom of the metal, exactly 107.88 gm.

If a solution of copper sulfate, CuSO_4 , is placed in the circuit, the weight of the copper deposited is to that of the silver as 107.88 to 31.78, that is, not in the proportions of the atomic weights (107.88 to 63.57) but in proportion to their equivalence, namely, the atomic weights divided by the valencies, thus,

$$\frac{107.88}{1} \qquad \frac{63.57}{2}$$

Similarly, the radicles liberated at the anode, or what amounts to the same thing, the acids (H_2SO_4 and HNO_3) formed at that point will be

$$\text{NO}_3 : \frac{\text{SO}_4}{2} = 63 : 48$$

The quantity of current required to liberate a gram-equivalent of any element or radicle is termed a *faraday*,¹ the gram equivalent of silver being 107.88, the experimental basis of the determination of the value of the unit

$$F = 96494 \text{ coulombs} = \frac{96494}{3600} = 26.8 \text{ ampere-hours}$$

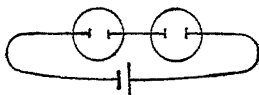


FIG. 4.

Inversely, the electrochemical equivalent of any substance is the amount in grams that is liberated by the passage of a coulomb.

The electrochemical equivalent of silver is

$$\frac{107.88}{96494} = 1.118 \times 10^{-3}$$

and the electrochemical equivalent of copper is

$$\frac{63.57}{2 \times 96494} = 0.329 \times 10^{-3}$$

Finally, these expressions can be condensed into the simple statement, that one faraday is required to set free one valency in any electrolyte, thus the faraday is a measure of valency.

The Periodic System of Mendeleeff.—Most of the elements are far from possessing the invariability of valency that is noted in the case of carbon; for instance, phosphorus is both trivalent and

¹The "faraday" must not be confounded with the "farad" The latter is a unit of capacity; the former a unit of electrolytic effect, as noted.

pentavalent; iron is bivalent in ferrous salts, and trivalent in ferric; manganese and chlorin assume almost all the degrees of valency from 2 to 7. In such cases, for all the compounds that are electrolytes, the liberation of a gram-equivalent will require as many faradays as the valencies of the liberated substance.

In the periodic system, one valency is arbitrarily chosen as a basis of classification, usually the highest degree, so that it is found that in the table the ordinates show the order of magnitude of the atomic weights, while the abscissas show valencies from 0 to 8.

The anomalies of the periodic table are somewhat numerous. Hydrogen, for instance, has no place, and if some of the rare elements are introduced, it is necessary to assign them valencies quite abnormal. Certain associations, such as oxygen with chromium, manganese with bromin, are not in accord with the marked differences in most respects between these elements. Finally, the general rule of the table is broken by the inverted relation between tellurium (127.6) and iodin (126.8), and between argon (39.9) and potassium (39.1).

In spite of these and some other defects, the periodic system has been of great advantage in putting in evidence many analogies of the elements showing, for instance, that fluorin resembles oxygen at the same time that it resembles chlorin; that tellurium resembles molybdenum at the same time that it has strong affiliations to selenium. The

Valence; 0	I	II	III	IV	V	VI	VII	VIII
Formula of typical oxid	M_2O	M_2O_2	M_2O_3	M_2O_4	M_2O_5	M_2O_6	M_2O_7	M_2O_8
He	Li	Gl	B	C	N	O	F	Fe, Co, Ni
Ne	Na	Mg	Al	Si	P	S	Cl	Br, Rh, Pd
Ar	K	Ca	Sc	Ti	V	Cr	Mn	
Kr	Rb	Sr	Yt	Zr	As	Mo	Br	
Xe	Ag	Cd	La	Sn	Sb	Te	I	
	Cs	Ba	Ln	Ce	Ho	Ds	Er	Os, Ir, Pt
	Tm	Eu	Gd	Tb	Ta	Tu		
Nt	Au	Hg	Tl	Pb	Bi	U		
		Ra		Th				

table has indicated the existence of several elements before their discovery, among which are scandium, gallium and germanium, and the existing gaps indicate the probability of further discoveries. It was well suited to introduction of the rare, non-active gases, by the simple addition of a column of zero valency, and even for the introduction of the radio-active elements as will be seen later, though these have complicated it in form, but confirmed the principle on which it rests.

Finally the order of magnitude which the table assigns to the atomic weights is entirely in agreement with the indications from atomic heats and transparency to x -rays, and so far is this true that we can feel confident that a given substance is an element when its atomic weight obtained by all three methods is the same.

SPECTRA OF THE ELEMENTS

Simple substances are distinguished from all other forms of matter by the character of the light emitted by them in the state of vapor. In the case of gases, the method of making them luminous is by transmitting through them an electrical discharge of high voltage, in tubes in which they are under very low pressure. Metals are examined by submitting them to action of the spark discharge or the electric arc, according to the degree of fusibility of the substance; finally, if the element is not a conductor of electricity, small portions of it are placed on platinum electrodes and a spark is dis-

Valence; 0	I	II	III	IV	V	VI	VII	VIII
Formula of typical oxid	M_2O	M_2O_2	M_2O_3	M_2O_4	M_2O_5	M_2O_6	M_2O_7	M_2O_8
He	Li	Gl	B	C	N	O	F	Fe, Co, Ni
Ne	Na	Mg	Al	Si	P	S	Cl	Br, Rh, Pd
Ar	K	Ca	Sc	Ti	V	Cr	Mn	I
Kr	Rb	Sr	Yt	Zr	As	Mo	Br	Os, Ir, Pt
Xe	Ag	Cd	In	Sn	Sb	Te	I	
	Sa	Eu	La	Ce	Ho	Ds	Er	
Nt	Tm	Hg	Yb	Tb	Ta	Tu		
	Au	Ra	Tl	Pb	Bi	U		

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charged through the mass, or in some cases the flame of hydrogen, or of the common illuminating

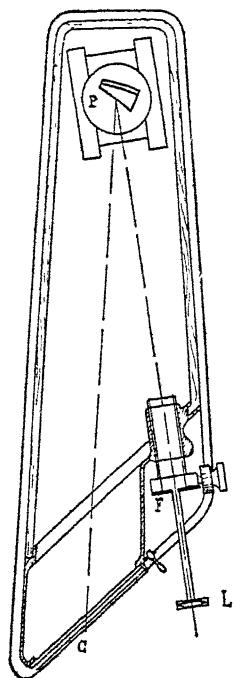


FIG 5—Féry's Spectrograph.

L Quartz lens

F. Slit.

P. Quartz prism, with curved faces, the posterior face being coated with mercury.

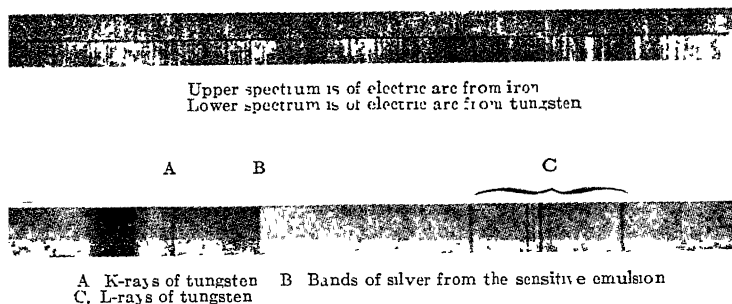
C. Frame for sensitive plate.

gas will answer. The radiations from the luminous substance are concentrated on a narrow slit, then dispersed by a prism, and the spectrum observed visually or recorded by photography. The spectrograph, which is displacing the spectroscope, differs from the latter by the addition of a photographic camera and by the use of quartz lenses instead of glass, as the latter absorbs the larger part of the ultraviolet rays, which are highly actinic. The spectrograph has also the advantage of allowing the study of the spectra at leisure and retaining the record of them, as is seen in the illustrations on Fig. 5A, which shows the superposed spectra of iron and tungsten about half natural size, obtained by the spectrography of Féry.

The spectra of the several elements differ in complexity, and are always simpler for the non-metals than for the metals; for many of

the latter it is sufficient to introduce a chlorid (if volatile) into the flame of a bunsen burner, or, in other cases, to volatilize an oxid in the electric arc. The spectrum obtained by the latter method is not pure, but as the lines of the metals are very numerous, and more intense than those of the non-metals, it is not difficult to identify the metal. What may be called the physiognomy of the spectrum should be observed, that is, the relative intensity of the

FIG 5A.



lines, the differences according to the mode of producing it, arc or spark. That each line, strong or weak, given by an element has a definite wavelength and, therefore, position, not to be confused with that from any other element, is the principle of the application of spectrum analysis, developed by Kirchhoff and Bunsen, a method of research that has been so fertile that most of the elements discovered during the last fifty years have been found by its means. To the spectroscope is also due a

demonstration of the essential unity of the composition of the universe, for rays indicating terrestrial elements have been found in the light of many of the stars and particularly of the sun. The exceptions to this uniformity are rare and, moreover, interesting. Thus, corona of the sun emits a ray corresponding to wave-length 5303, which has not yet been identified with any known element, and is ascribed to a supposititious element *coronium*. The spectra of the nebulas are as yet not fully explained, but most of them show lines of hydrogen, helium and of an unknown element, termed provisionally, *nebulium*, with a ray of wave-length 3727, and possibly also 4959 and 5007.¹

So far all the elements found in the earth have not been found in the sun, which may be due to the unequal sensibility of the spectroscope to the several types of lines. This sensibility is very high for some elements, such sodium and lithium, which can be detected in quantity as small as a few millionths of a milligram, but in the case of other elements, the delicacy is much less, often because the lines are masked by impurities, so that before using the spectroscope, the substance to be tested

¹ It is possible to determine the atomic weight of a gas known only by a spectrum ray, by utilizing a principle of the kinetic theory, according to which the width of the line bears a relation to the speed of movement of the luminous particles in a luminous gas, and to the atomic mass. Buisson, Fabry and Bourget studying line 3727, in the spectrum of the nebula of Orion, found for nebulium an atomic weight of about 3. (*Jour. Soc. de Physique*, 1914.)

must be subjected to chemical purification. In proportion as the purity of the substance increases, the lines become more distinct and numerous, the first appearing, being not always the most striking of these seen in the pure spectrum. The most enduring of the lines of any element have been termed *ultimate rays*, by de Gramont, who has determined them for many of the elements.

Series Spectra.—The position of the lines of a given spectrum, independently of the state of mixture or combination of any element, will depend on certain physical conditions, such as the intensity of the magnetic field and the pressure. Thus, in the arc the lines of a given element are displaced towards the red; in the open arc by a very slight amount, but more marked when the arc is in a closed vessel with an air pressure of fifteen atmospheres. The most remarkable property is that the rays of a given element are not all equally affected by these changes of conditions, being capable of classification in series, by reason of their differing sensitiveness to changes in the magnetic field and pressure. These series have markedly different aspects, some lines being diffuse and others sharply limited, obeying in this respect the laws of position that can be expressed in an empirical formula, the formula of Rydberg, which is

$$n = n_0 - \frac{N_0}{(m + p)^2}$$

in which n is the number of the waves (or the frequency of oscillation, which is the inverse of the

length of the wave) of the rays of the series, N_0 , a constant value for the spectra, 109675, m , one of the whole consecutive numbers, n_0 , the limit towards which n tends when m becomes infinite, and p , a number smaller than unity, characterizing each of the series.

Summarizing: A pure spectrum is decomposable into a principal series and several subordinate ones, almost as a complex sound is divisible into its fundamental note and its harmonics, but with less precision, for it often occurs that important lines cannot be placed in the series groupings. Thus, calcium gives four very strong lines that are not yet classifiable. In spite of these exceptions, the existence of these series spectra suggests that what we call elements may be after all not simple substances, but complexes, having an internal structure and not wholly non-convertible.¹

The phenomena of radio-activity, which will next be taken up, furnishes a direct proof of the relations that exist between certain elements.

RADIOACTIVITY AND ATOMIC DEGRADATION OF THE ELEMENTS

Discovery of Radioactivity.—It is known that a solid body interposed in the path of the cathode rays transforms them into x -rays, for instance, the glass walls of Crookes tube emit x -rays, becoming

¹ For a detailed study of spectroscopy, Marshall Watts' *Introduction to the Study of Spectrum Analysis*, and G. Urbain's *Introduction à l'étude de la Spectrochimie*, may be consulted.

at the same time phosphorescent. Some time after the discovery of the x -ray, Henry Poincaré suggested that inasmuch as the phenomena of emission and phosphorescence are inter-related, a phosphorescent substance should reciprocally emit x -rays. To test this view, H. Becquerel, in 1895, made experiments by exposing phosphorescent

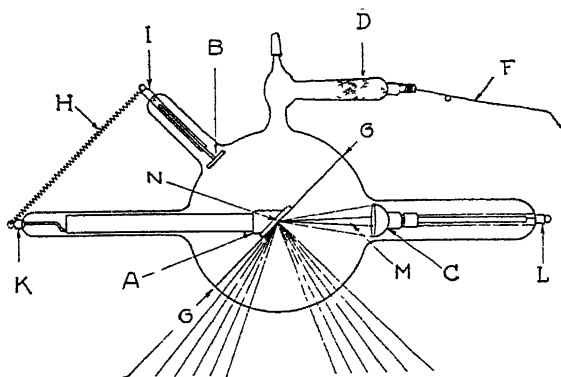


FIG. 6— x -ray tube

A, anode, *B*, assistant anode, *C*, cathode, *D*, regulating chamber *F*, regulating adjuster, *G*, hemisphere, *H*, connecting wires, *I*, assistant anode cap, *K*, anode cap; *L*, cathode cap, *M*, cathode stream, *N*, focal point.

objects, in full light, to photographic plates wrapped in black paper, hoping to detect the x -rays which are capable of penetrating the paper and would affect the plate if any were emitted. The result was blank except with uranium potassium sulfate. Not only did this affect the protected plate, but the action was carried on for a long time in perfect darkness. It was evident that the action was due to

the salt, and that the general illumination and the phosphorescence were not causes. Some months later, Madame Curie undertook the investigation and studied it quantitatively, by an electrometric apparatus, a simple form of which is shown in Fig. 7.

The upper plate A, insulated and electrically charged, carries a slip of gold-foil, the angular deviation of which can be read on a graduated arc. The plate B is grounded. Upon it is placed a thin layer of the substance to be tested. The radiation from this substance renders the air between the two plates more capable of conducting electricity, and the gold-foil slip falls in consequence of this discharge,

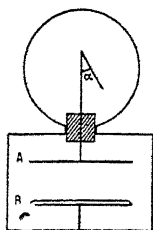


FIG. 7.

the rate of fall being in direct proportion to the intensity of the radiation. It was demonstrated that the intensity of the radiation is dependent on the uranium present, and not on any of the other elements; the property is purely atomic, and is possessed in greatest degree by uranium itself.

As a remarkable exception, however, it was found that the mineral pitchblende, an impure uranium oxid (containing among other elements thorium and lead) has a higher radioactivity than metallic uranium, which indicated the presence of another element of more powerful radioactivity. Trials with various fractions from chemical treatment of pitchblende enabled this element to be traced more closely, and Madame Curie, fractionating several

kilograms of the mineral, in association with Pierre Curie and G. Bémont, succeeded in localising and concentrating the radioactivity in a group of alkali-earth metals, and finally indicating an element with a radioactivity about three million times as strong, weight or weight, as that of uranium. The proportion of the new element, *radium*, present was 100 mg. per 100 kilos of the mineral. Radium gives a spectrum analogous to those of the alkali-metals and has a high atomic weight, but it differs from all other elements so far known in emitting spontaneously and continuously, a radiation that is equal to 118 calories per hour for a gram of the element, whether free or combined.

By these researches a new method of investigating the elements was introduced, the electrometer, an instrument several thousand times more delicate than the spectroscope.

Analysis of the Radiations.—Radium emits a complex radiation, in which three types have been found, termed respectively, alpha, (α) beta (β) and gamma (γ), the order of penetrating power being that of the titles. The alpha rays are but feebly penetrating, being composed of material particles charged with positive electricity; the beta rays are of the same nature as the cathode rays, and are electrons charged with negative electricity, and have no mass, or almost none. The gamma rays are very penetrating, and of the same nature as the x-rays, that is, are due to vibrations of the same order of those of light, but of wave-length about

TABLE
RADIOACTIVE

		At wt	
Uranium I		238 5	
(5 10^9 years)		↓ α	
Uranium X		234 5	
(24 6 days)		↓ β	
Uranium X ₂		234 5	
		↓ β]	
Uranium II .		234 5	
(10 ⁶ years)		↓ α	
Ionium		230 5	
(10 ⁵ years)		↓ α	
Radium . . .		226 5	
(2000 years)		↓ α	
Radium emanation		222 5	
(3.86 days)		↓ α	
Radium A		218 5	
(3 minutes)		↓ α	
Radium B . . .		214 5	
(26 7 ₂ minutes)		↓ β	
Radium C ₁ . . .		214 5	
(19.5 minutes)		↓	
		↓	
Radium C' . .	214 5	Radium C ₂ .	210 5
(10 ⁻⁶ second)	↓ α	(1 4 minute)	↓ β
Radium D	210 5		
(16 years)	↓ β		
Radium E . .	210.5		
(5 days)	↓ β		
Radium F	210.5		
(136 days)	↓ α		
Radium G	206 5		
(inactive)			

A

TRANSFORMATIONS

Thorium (3 10^{10} years)	At wt 232 4 $\downarrow \alpha$		
Mesothorium (5 5 years)	228 4 $\downarrow \beta$		
Mesothorium II (6.2 hours)	228 4 $\downarrow \beta$		
Radiothorium (2 days)	228 4 $\downarrow \alpha$		
Thorium X (3 7 days)	224 4 $\downarrow \alpha$		
Thorium emanation (53 seconds)	220 4 $\downarrow \alpha$		
Thorium A (0 14 second)	216 4 $\downarrow \alpha$		
Thorium B (10 6 hours)	212 4 $\downarrow \beta$		
Thorium C (55 minutes)	212 4 $\downarrow \beta$		
Thorium C ₂ (10 ⁻¹¹ second)	212 4 $\downarrow \alpha$	Thorium D (3 1 minutes)	208 4 $\downarrow \beta$
Thorium D ₂ ?	208 4 $\downarrow \beta$		
Thorium E (inactive)	208 4		
		Actinium 226 5 $\downarrow \beta$	
		Radioactinium (19 5 days) $\downarrow \alpha$	226 5
		Actinium X (10 2 days) $\downarrow \alpha$	222 5
		Actinium emanation (3 9 seconds) $\downarrow \alpha$	218 5
		Actinium A (0 002 second) $\downarrow \alpha$	214 5
		Actinium B (36 1 minutes) $\downarrow \beta$	210 5
		Actinium C (2 15 minutes)	210.5

NOTE.—Some of the atomic weights given in this table are not exactly those now adopted under international agreement, but the differences are slight and do not affect the principles which the table is intended to set forth. The weights here given are of earlier date.—Fr

one-ten-thousandth that of ordinary visible light. The alpha and beta rays are of the nature of matter, the gamma rays of energy. All these rays possess high velocity similar to that of light but less. The alpha and beta rays, carrying electrical charges, are capable of being diverted in a magnetic field, the diversion being of opposite character, since they are oppositely charged; the gamma rays carrying no charge, are not influenced by the magnet. These differences permit of separation of the different rays by the selective action of a magnetic field.

Mean Duration of Life of the Radioactive Elements. Rutherford and Soddy have given an explanation of these facts, now generally accepted, and moreover in some cases verified by experiment, namely, that an atomic disintegration occurs. A radioactive element is a substance undergoing evolution; it is disintegrating into other substances, stable or unstable. It is an explosive, which, in bursting, throws out one or more particles inferior in weight to its atoms, also rays, α , β , γ , which are ultimately resolved into heat. The explosion, however, is not instantaneous, or rather, does not involve the whole mass at the same moment. Of the great number of atoms that compose the radioactive substance, most are inert at any given moment, and only a few become suddenly active, for causes not yet known. The emissions are provoked by the development of radioactivity in the atoms, and it may be assumed that the number is in proportion to the radioactivity itself. The action diminishes with

time, at such a rate that diminution at any instant is proportional to the intensity at that instant.

Let I_0 be the intensity at the instant from which time is counted: and I_t the intensity at any time, t , that is t seconds after the time when the radiation is I_0 , and e the basis of the Napierian system of logarithms (2.718), and l a constant (see below), then

$$I_t = \frac{I_0}{e^{lt}}$$

The number of radioactive atoms will follow the same law of decrease in which N_0 is the number of

$$N_t = \frac{N_0}{e^{lt}}$$

atoms at the instant from which time is reckoned, and N_t the number of atoms at the time t .

The magnitude of l being very different for the different radioactive elements serves to differentiate them fully from each other, but we can replace it usually by its reciprocal,

$$\theta = \frac{1}{l}$$

(in which θ represents temperature), a magnitude more expressive since it represents the sum of all the ages of radioactive atoms, divided by the total number of atoms existing at a given instant. This is the mean duration of the life of the element, being for radium, 2500 years.

Radium Emanation.—Radium and its compounds, confined in a closed vessel, disengage a substance detectable by the electric conductivity that it

imparts to the atmosphere of the vessel, but this must not be confused with radium radiations, since it is displaceable as a gaseous substance. It is in fact a radioactive gas becoming liquid at -153° , and a new element, which exhibits a characteristic spectrum and is called *niton*. It might easily escape detection but for its continual production from radium, for its life is only about 92 hours on the average.

Radioactive Transformations.—The spontaneous transformation of radium into the emanation (niton) is only a step in a series of which uranium is the first point. Uranium produces radium, which is never found in other than uranium containing minerals, but uranium has a life of about eight million years, hence the transformation of it into radium is much more slow than that of radium into its emanation.

From the mean duration of the life of the emanation and the quantity of heat that it disengages, we can calculate the amount of energy set free by an atom, an amount quite considerable in proportion to the mass that is concerned in the action, and which is such that the degradation of a given volume of radium emanation liberates about three million times more calories than the explosion of an equal volume of detonating gas (2 volumes of hydrogen to 1 of oxygen).

To reverse the course of such a phenomenon, and reconstitute the degraded element, a vast amount of energy would be needed, and it has been so

far impossible to divert or accelerate the spontaneous transformation of an element, the constant λ having shown itself to be independent of all conditions of temperature, electric discharges, influence of a magnetic field, etc. Thus may be explained the failure of all the older efforts at transmutation.

Radium emanation in its turn is disintegrated, as it is radioactive, and forms a series of elements, each of which is distinguished from the others by the mean duration of its life and by the composition of the radiation that it emits. Three series are now known, two derived from uranium and thorium, respectively, elements long known, and the third from *actinium*, discovered later by Debierne, in pitchblende. The actinium series shows a steady fall in activity from the beginning to the end of the series, the final products being inactive.

Atomic Weights of Radioactive Elements.—If, after having isolated the radium emanation, its spectrum is observed for a limited time, it will be noted that during the rapid degradation, the characteristic lines fade out steadily and are replaced gradually by a line characteristic of helium. This important observation by Ramsay and Soddy in 1903 furnished the first instance of the spontaneous formation of an element already known, and not radioactive. The experiment showed that a connection exists between the emanation and helium, which was more exactly determined later. It was found, by several physical methods, notably the deviation of the alpha rays by a magnetic field, that the mass of each of the

projected particles of which these rays consist is equal to four times that of hydrogen, that is, to the atomic weight of helium. Rutherford has inferred that the atoms of ordinary helium are merely alpha rays deprived of their active powers.

The following experiment proves this. If the radium emanation is sealed in a small glass tube, the walls of which are not thicker than 0.01 mm., the atoms of helium, projected with high velocity, under the temporary form of alpha rays, pass through these walls, and, by reason of the highly characteristic and delicate spectroscopic features of helium, this substance can be found at the expiration of a few hours in the space surrounding the thin-walled tube. The formation of helium from the emanation is, therefore, established, as well as the transitory condition of the helium as the alpha rays. Now, if the alpha particle is an atom of helium, the atom that emits it should lose 4 units of its weight. This is demonstrated by the following equation, in which the atomic weights of the three elements concerned have been determined by direct methods, to wit: A chemical method for radium, vapor density for helium, velocity of diffusion for the emanation.¹

¹ The velocities of diffusion or flow of two gases under the same pressure are inversely proportional to the square roots of their densities. This ratio gives a method of determining the molecular weight of a gas by comparing its velocity of diffusion with that of hydrogen. It is known, moreover, that radium emanation is monatomic and has zero valency, therefore, without chemical affinity, as are all the gases of its group (the so-called "noble" gases) and its atomic and molecular weights are the same.

Radium = Emanation + Helium

$$226.5 = 222 \text{ 5} + 4$$

In the same way, there is a loss of three particles in the transformation of uranium to radium.

Uranium = 3 Helium + Radium

$$238.5 = 3 \times 4 + 226.5$$

To be exact, we can distinguish two types of atomic degradation, those which occur with emission of alpha rays and a diminution of 4 units in the atomic weight, and those accompanied by emission of beta rays—the mass of which is insignificant¹—and which give rise to atoms differently constituted from the original atoms, but without change of atomic weight. Examples of this will be seen in Table A, pp. 52, 53.

Positions of the Radioactive Elements in the Periodic System.—How does the periodic classification adapt itself to these numerous new elements? To place them it is not alone necessary to know their respective atomic weights, for these are all high, and assignable to a position in the table in which there are many gaps, but it is necessary to determine the chemical characters of each element, that is, the family or group to which it belongs. This problem, which seems so difficult in dealing with substances that are obtainable in only very minute quantities, has been solved in several cases by a method based on the data of isomorphism.

¹ About $\frac{1}{1700}$ of that of an atom of hydrogen.

Take, for instance, the determination of the group to which thorium X belongs. Different metallic salts are crystallized in association with a salt of this substance, and by means of the electrometer, the crystals in which the thorium X is located can be detected. If the thorium X remains in the mother liquor, that is, is not associating with the crystalline mass, then it has no resemblance to the metal under comparison. If, on the other hand, the electrometer shows that it has distributed itself between the crystalline mass and the mother-liquor, then the salts are isomorphous. Now, of different salts tried, those of barium alone show the power of crystallizing with thorium X and the latter is, therefore, an alkali-earth metal with an atomic weight of 224.4. It should, therefore, be placed below barium and on the same line with thorium. Generalizing from these facts, Fajans and Soddy have proposed the following two rules for the succession of radioactive elements:

1. When there is a loss of an alpha particle, the element loses four units of its atomic weight, and retrogrades two columns in the periodic table (from the zero group to the 6th group when the element is monovalent). Thus, tetravalent thorium passes into bivalent mesothorium I; bivalent radium passes into non-valent emanation (niton).

2. If the degradation is caused by the loss of a beta particle, the element produced finds place in the immediately adjacent family and the valency increases without change of atomic weight.

Isotopes.—One of the results of these shiftings to right or left in the table, is that the same place may become the assignment of several elements. An example is thorium X (224.4), an alkali-earth metal, the assigned place of which is also occupied by radium (226.5). According to Fajans, this is a normal and not an abnormal condition, and if we carry out the principles of the two laws just stated, in application to all the elements of Table A, they will take their place in the periodic classification as indicated in Table B, p. 62, which is an appendix to Table A.

Each of the places in the periodic classification is not the domain of a single element, but of a group of elements, the members thereof being termed *isotopes*. They resemble each other to the highest degree chemically. They are not merely analogous, as are the metals of the potassium group, or merely very difficult to separate, as are the associates of lanthanum, but they are practically incapable of separation by known chemical means, when they are once intermingled. The separation of them is only possible by physical methods, based on the differences in their atomic weights, for instance, in the case of gases, by the difference in the rate of diffusion.

It has not yet been proved that this conception is applicable to the elements with very low atomic weights¹; it is not impossible that some recent and

¹ For some investigations into possible isotopy of chlorine, see a paper by W. P. Harkins, *Science*, [n.s.], 1920, 51, 289—Tr

TABLE B.—POSITION OF THE RADIOACTIVE ELEMENTS IN THE PERIODIC SYSTEM

0	I	II	III	IV	V	VI
218.5 Ac Em 220.4 Th Em 222.5 Ra Em	197.2 An Ac X ₂ 218.5 Th X ₂ 220.4 Ra X 222.5	200.6 Hg Ac X 222.5 Th X 224.4 Ra 226.5 Mes Th I 228.4	204.4 Tl 208.4 Th D 210.5 Ra C ₂ Ac 226.5 Mes Th II 228.4	207.1 Pb 208.5 Ra G 208.4 Th D ₂ 210.5 Ra D 210.5 Ac B 212.4 Th B 214.5 Ra B	208.5 Bi 208.4 Th E 210.5 Ra E 210.5 Ac C 212.4 Th C ₁ 214.5 Ra C ₁	210.5 Ra F 214.4 Th C ₂ 214.5 Ra C 214.5 Ac A 216.4 Th A 218.5 Ra A
					UX ₂ 234.5	U II 234.5 U I 238.5

very delicate experiments on which the conception rests may be subject to revision, but the general principle seems to be established by the following remarkable results.

The place of lead in the table is a point at which the inactive substances of three series of degradation converge. If these are really isotopes and inseparable from lead, the atomic weight of the metal will depend on its source, that is, the proportion of isotopic elements that are associated with it. Now the accepted atomic weight of lead (207.2) is intermediate to those of the isotopes in Table B. Several investigators have recently determined the atomic weight of specimens of lead from different sources, and have obtained figures appreciably different, according as the metal was extracted from radioactive or inactive minerals. The following figures quoted from Richards and Lemberg will illustrate the point.

Lead from Carolina pitchblende. . .	206.40 ± 0.05
Lead from Joachimsthal pitchblende. . .	206.57 ± 0.02
Lead from carnotite (Colorado). . .	206.59 ± 0.01
Lead from thorianite (Ceylon) . . .	206.82 ± 0.01
Lead from pitchblende (Cornouailles) . . .	206.86 ± 0.02
Lead from galenite	207.14 ± 0.01

The following figures were obtained by Maurice Curie.

Lead from uraniferous minerals . . .	206.36 to 206.64
Lead from galenite.	207.01
Lead from monazite	207.08

Finally, Soddy and Hyman obtained for lead from Ceylon thorite, the atomic weight 208.4.

Table B indicates analogous differences for bismuth, thallium and uranium, but no verification of such relations has yet been obtained.

STRUCTURE OF THE ATOM

The Atomic Number.—According to the rule of Fajans and Soddy (p. 60), a transformation of a radioactive element, with loss of a β ray, shifts the transformed element towards the right hand of the periodic table and places it in the group immediately adjoining its former group and of higher valency, while the loss of an α ray, shifts the element in a contrary direction. Hence, the charge gained or lost by an element determines its place in the periodic table. The electron β is inseparably connected with a unit charge of negative electricity, and the α particle is known by direct measure to carry two unit charges of positive electricity. It will be sufficient then to enumerate in the natural order of numbers, beginning with hydrogen as 1, the places of the elements in the increasing order of their atomic weights, to give to each a new coefficient—*atomic number*—the great importance of which has been shown by Moseley in a study of the rays characteristic of the elements.¹

Relation Between the Atomic Number and the High-frequency Spectra of the Elements.—The terms “characteristic x -rays” and “secondary rays” have been applied to the radiations emitted by elements

¹ Moseley, *Phil. Mag.*, 1913, **26**, 1024; *ibid.*, 1914, **27**, 703.

when they are struck by rays coming from the *x*-ray bulb. These secondary rays, like the *x*-rays themselves, consist of vibrations of extremely short wave length and high frequency, with penetrating power that increases with the increase of the atomic weight of the element upon which the *x*-rays impinge. It has been discovered by test of their penetrating powers, that they are characteristic for each element, and can be classed in at least two series, termed respectively, series *K* and *L*. The differentiation of the several rays can be clearly made by a new spectroscopic method, which consists in reflecting them from the surface of a crystal, which is a natural grating much finer than can be made by mechanical processes (see appendix).¹

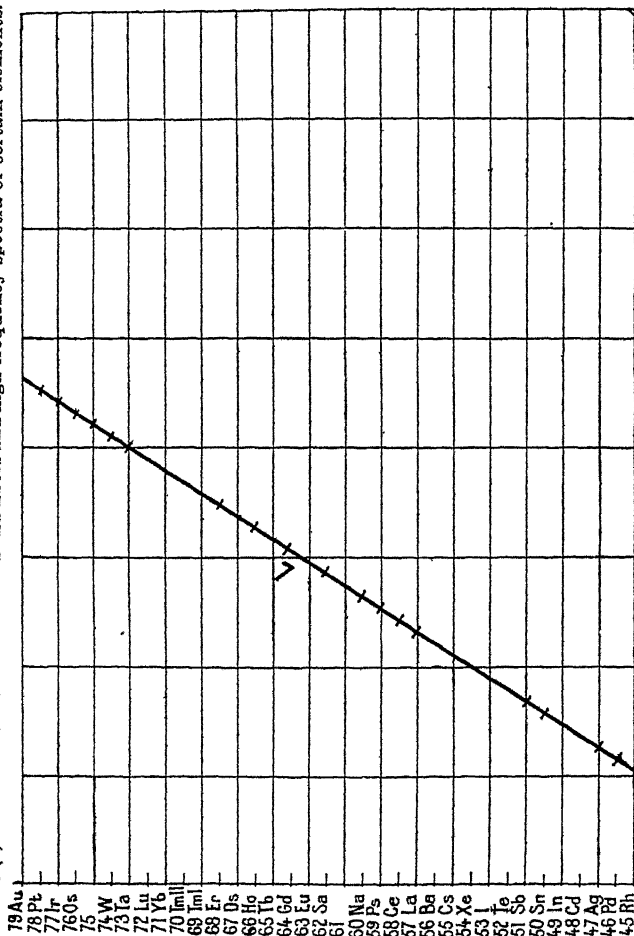
The spectra of these secondary rays are much less complex than the ordinary luminous spectra, as is illustrated by the *x*-ray spectrum of tungsten, figured by de Broglie, in *b*, plate 1. These spectra are made up of a few lines which are shifted regularly from one element to the other in such a manner that the wave-length changes according to a law expressed in the following equation in which *v* is

$$v = \frac{1}{\lambda} = A(N - B)^2$$

the frequency of vibration, λ the wave-length, *A* and *B* certain constants, and *N* a whole number characteristic of each element, identified with the atomic number as indicated in Fig. 8.

¹ See de Broglie, *Jour. d. Physique*, [5], 1914, 4, 101, 265, and *Revue Scientifique*, 1915, 577.

FIG. 8 (1).—Relations between the atomic numbers and high-frequency spectra of certain elements.



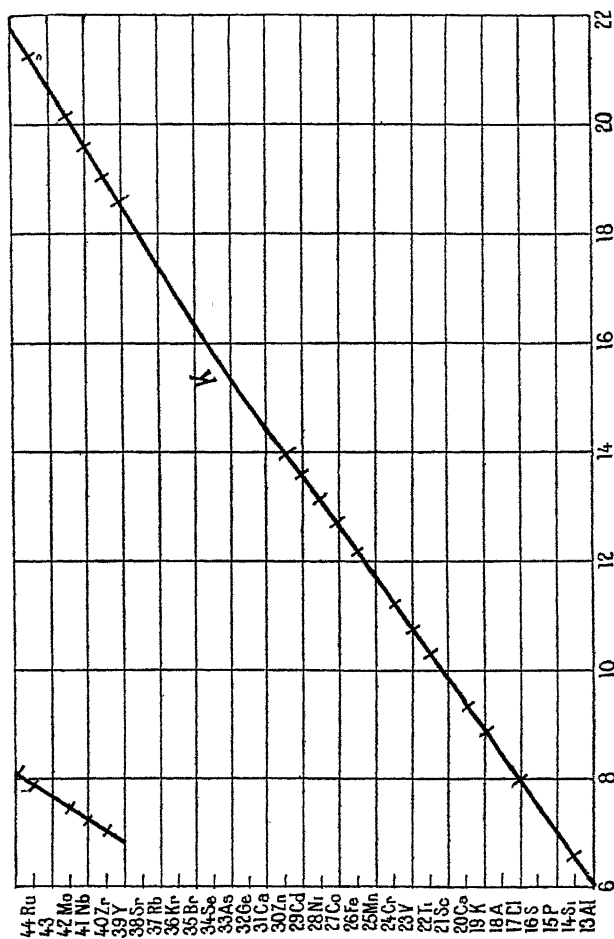


Fig. 8 (2).

Until the present, experiments have only been practicable with the elements ranging from aluminum to gold, both inclusive, but they are sufficiently demonstrative to be applicable to any element. Assigning to aluminum, the number 13, which is derived from the table on page 42, starting with hydrogen as unity, the whole series of consecutive numbers reproduces exactly the periodic classification, even to its blanks and anomalies. Thus, cobalt (58.9) precedes nickel (58.7) by reason of the chemical resemblances between cobalt and rhodium, on the one hand and nickel and palladium on the other. The vacant places are here more suggestive of new elements than under the older arrangement; three only of them, 43, 61, 75, are available within the limits of aluminum and gold, and one of these is among the rare earths group. It must be borne in mind that the same number may apply to several isotopic elements. It seems, therefore, definitely, that it is the number and not the atomic weight which is the actual base of the periodic classification.

STRUCTURE OF THE ATOM.¹ The present day views are here briefly set forth, it being premised that many modifications may take place as results of investigations.¹

Electrons.—All atoms contain a common constituent, the electron, the discovery of which resulted especially from studies made of the phenomena of the Crookes tube. Differing completely from light, the cathode rays are made up of distinct corpuscles,

¹ Sir J. J. Thomson, The Atomic Theory, Romanes lecture, 1914.

of extremely minute mass, about $\frac{1}{1700}$ of that of the atom of hydrogen. These corpuscles are negatively charged and have a high velocity, approximately 50,000 kilometers per second, exhibited in the electrization of all gases, also by the reflection of rays of ultra-violet light from a metallic surface, in the radiation of radioactive bodies (β rays), in the incandescence of metals, and even in some exceptional chemical reactions. The velocity is dependent upon the electric potential influencing them, but the charge and the mass are always the same, whatever may be the circumstances of their liberation. The electron is, therefore, a universal constituent of matter.

The Positive Nucleus.—To compensate for the negative charges of the electrons, the neutral atom should contain a positively charged mass, which Rutherford considers as reduced to a very minute central nucleus about 0.0001 of the diameter of the whole atom. Around this positive nucleus, in which is concentrated the individuality of the atom and almost its entire mass, the electrons circulate, in number about equal to the half of the atomic weights. Helium (at. wt. 4) has 2 electrons, carbon (at. wt. 12) has 6, oxygen (at. wt. 16) has 8, but hydrogen departs from the rule having one electron and the positive nucleus. Moreover, though all the electrons are identical among themselves, they probably have not exactly the value as constituent particles, for it seems illogical to assume the same origin to the electrons that are

emitted in such a peculiar transformation as that of the radioactive substances (β rays) as to the electrons that are liberated in such a simple change of valency as occurs when ferrous salts become ferric. The electrons in the former instance, probably come from a deeper and more essential part of the atom than do those that are emitted in the latter case.

It can also be assumed that the electrons are arranged in several concentric groups, and even that they may enter in part into the central nucleus, the positive charge of which may be merely an excess over the negative charge of the included electrons, that is the *algebraic sum* of the element. The electrons of the exterior zone, more mobile and less strongly bound to the mass, will be more sensitive to external influences, and the properties of which they are the basis will be modified when the atom is united to another atom. These external zones will be the domain of the ordinary physical and chemical properties, which vary with the atomic weight, and which vary periodically, (see p. 35), as if an accumulation of electrons, correlated with the increase of atomic weight, terminated by developing a critical instability, periodically upset to give way to a more stable condition. To the internal regions of the atom will belong the strictly atomic properties, not modified by combination, such as the secondary radiation, this not manifesting any periodicity.¹

¹ For further discussion of theories of the structure of the atom, see papers by Irving Langmuir, *Proc. Nat. Acad.*, 1919, 5, 252 and *Jour. Amer. Chem. Soc.*, 1919, 41, 868.—Tr.

CHAPTER V

PROPERTIES AND THEORIES OF SOLUTIONS

A maxim of the alchemists, confirmed by all modern experience in chemistry was that substances react only when dissolved. Chemical action does not take place at a distance; it requires intimate contact, that can only be realized between dry substances by high compression, but it is usually brought about by the intervention of a third substance, a dissolving liquid. This condition is so important that substances, such as lime and carbon dioxid or hydrogen and oxygen which have high mutual affinities will not combine unless some water is present.¹

We cannot by any general rule, as yet, predict if a given solid is soluble in a given liquid, but usually there is some chemical resemblance though often slight, between the solvent and the substance dissolved (solvend). Thus mercury is a metal and it dissolves only metals; water dissolves a great number of mineral substances and not a very large number of organic substances, its action being

¹ Fusion will in many cases bring about combination without the presence of any third substance, but it has been shown that some gaseous mixtures such as carbon monoxid and oxygen will not react if perfectly dry.—Tr.

especially noticeable on those substances which have some resemblance to its molecular structure, such as the organic acids, alcohols and carbohydrates, which contain the group HO, hydroxyl. In the same way, the liquid hydrocarbons dissolve the solid hydrocarbons. In this respect, solution differs distinctly from combination, as the latter is usually more active in proportion as the substances are different. Solution also differs from combination in not being governed by the law of definite proportions, since the action may take place in a wide range of proportions, and lastly, solution when it is not accompanied by chemical action as a secondary effect, takes place with reduction of temperature (endothermic) while most true chemical actions are accompanied by heat disengagement (exothermic).

The consideration of dilute solutions will be first taken up, as these are applicable to the determination of molecular weights, then the concentrated and saturated solutions and lastly, the solid solutions.

DILUTE SOLUTIONS

Cryoscopy, Ebullioscopy, Osmotic Pressure.

Cryoscopy. (Determination of Freezing Point). The freezing point of a solution is always lower than that of the pure solvent, the amount of depression being influenced by the nature of the solvent, the concentration of the solution and the molecular weight of the dissolved substance.

The laws of this phenomenon were early indicated by several investigators, notably the English scientist, Blagden, in 1788, but F. M. Raoult was the first to demonstrate for non-saline substances, in dilute solution, the principle in the following form, simple and widely applicable, which serves as a method for determining the molecular weights of substances in solution.

Raoult's Laws (1) *In the case of a given substance, the depression of the freezing point, that is, the difference between the freezing point of the pure solvent and that of the solution, is proportional to the concentration of the solution.*

2. *Different substances dissolved in equal numbers of molecules in the same kind of solvent, depress the freezing point in equal amount.*

Let D represent the amount of depression of the freezing point corresponding to a weight w of a given substance, dissolved in 100 grm. of solvent, D' the depression corresponding to the weight w' , of the same substance. Then, by the first law

$$\frac{D}{D'} = \frac{\frac{w}{100}}{\frac{w'}{100}} = \frac{w}{w'}$$

By the second law, if w' is equal to M gram-molecules dissolved, D' becomes a constant appertaining to the solvent employed and

$$D = K \frac{w}{M} \text{ from which } M = K \frac{w}{D}$$

In other words, it is the number of molecules of the substance dissolved in the unit volume of solvent that determines the depression of the freezing point.

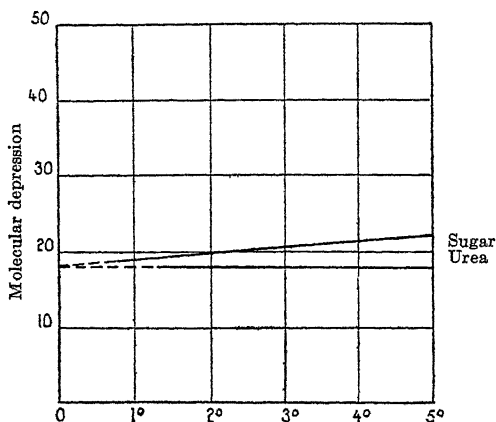


FIG. 9.—Depression of freezing-point of water.

Determination of K .—If Raoult's laws were rigorous for concentrated solutions, the determination of K could be made by dissolving a gram-molecule of a substance the molecular weight of which is known in a given solvent and measuring the depression, which would be equal to K , but such concentrations are not easy to measure and often impossible to obtain, on account of the low solubility of the substance. Instead, therefore, a minimum weight of a known substance is dissolved in a given solvent and from the observed depression is deduced

$$K = M \times \frac{D}{w}$$

The measurement, repeated with several solutions and with decreasing concentration, can be represented on the ordinates of a diagram, of which the abscissas are the concentrations, or what amounts to the same thing, the depressions, from which, by extrapolation, the molecular depression at the origin can be deduced, that is, the value of K at infinite dilution, at which point the laws of cryoscopy are exact. The following data are obtained with the usual solvents.

	Freezing point	K
Water.	0 0	18.5
Acetic acid.	16 7	39 0
Phenol.	39 0	74.0
Benzene.	5 5	49 0
Ethylene bromid..	9 7	118 0
Nitrobenzene.	5 3	70 7

The value of K being known for a given solvent, a weight W , of a substance of the molecular weight is to be determined in 100 grm. of the said solvent, and the depression of the freezing point corresponding to D , recorded. Then

$$M = K \frac{w}{D}$$

It is best to make several determinations with decreasing concentrations, and deduce the value of M at the point of infinite dilution, that is, under the conditions in which the value of K was fixed.

Procedure.—A form of apparatus used is shown in Fig. 10. The solvent is placed in the tube *A*, separated from the cooling material *R*, by a tube a few millimeters wider. The temperature of the cooling material is kept a few degrees below the estimated freezing point, and when the thermometer *T* (which should be sensitive to $\frac{1}{50}$ of a

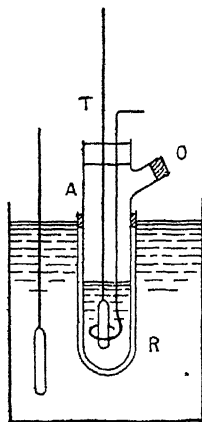


FIG 10

degree) indicates a temperature a little below that of the assumed freezing point, the super-fusion which often occurs in such cases, is broken by introducing into *A* a crystal of the substance under test. This crystal should have been obtained by freezing some of the substance in a separate vessel. The mixture is stirred and the temperature will rise to the true freezing point, which is read on the thermometer. The operation conducted with a

solution of known concentration indicates a temperature θ' ; the depression sought is expressed:¹

$$D = \theta - \theta'$$

In precise experiments it is necessary to avoid a great difference between the temperature of the solution and that of the cooling bath; the latter



FIG. 11.



FIG 12.

¹ The difference D being the important point, absolute accuracy of the thermometer is not essential, provided it is very sensitive. Thermometers have been made especially for these determinations with a very slender stem, in which the volume of the mercury can be varied at will. Such instruments are adapted to measure with precision differences in regions of temperature quite distant from each other. One of the simplest forms of this type is the differential, automatic thermometer of Ruelle of Paris. Fig. 11 shows how the excess of mercury is expelled as desired by heating; Fig. 12 shows how this mercury can be drawn back into the reservoir by cooling.

should be kept at about 0.1 below the freezing point. These extreme precautions are not usually needed and a single test will often suffice to determine the relative magnitude of the molecular weight, which is the problem most generally presented in organic chemistry. The molecular weights of many non-volatile bodies, which are not amenable to the vapor density method have been determined by cryoscopy. Among these substance, is xylose, a carbohydrate which cannot be volatilized without complete decomposition, but which is very soluble in water. Its approximate molecular weight, ascertained by cryoscopy, is 154, and its empirical formula, established by elementary analysis, CH_2O . The molecular weight calculated from the empirical formula will be 30, but the cryoscopy data show that the weight should be about five times this amount, hence the formula is $\text{C}_5\text{H}_{10}\text{O}_5$ giving a molecular weight of 150.

Ebullioscopy. (Determination of boiling point.) The tension of any liquid at a given temperature is depressed by a substance in solution, according to laws essentially the same as those of cryoscopy. The depressions of tension of dilute liquids are in proportion to the raising of the boiling points. Designating by D the difference between the boiling point of the solution and that of the pure solvent, we will have

$$D = K \frac{w}{M}$$

w being the weight of the substance in 100 grm. of the solvent and M the molecular weight. This principle, analogous to cryoscopy, is applicable to many cases, but is not extensively employed.¹

Analogies between Dilute Solutions and Gases. Osmotic Pressure.—Three good reasons are known for regarding the physical structure of dilute solution (upon which depend the phenomena of cryoscopy and ebullioscopy) as comparable to that of gases, in the sense that the dissolved substance is distributed through the solvent in the form of free and mobile molecules in the same manner as the molecules of gases are free and mobile, and perhaps more mobile yet in the empty space in which they are contained.

The first suggestion of this relation was made by Gay Lussac, who was led to it by observing the common property of liquids and gases to diffuse freely, but the principle was not precisely set forth until 1877, when Van't Hoff based it on observations made by the botanist, Pfeffer, who showed that vegetable cells examined under the microscope, swell when submerged in pure water and shrivel in strong saline solutions. In each case, the action is due to the tendency of the respective concentrations within and without the cell to equalize themselves. The texture of the cell-membrane permits

¹ The constant K is related to the absolute temperature and to the latent heat of fusion or of vaporization, by a thermodynamic formula due to Van't Hoff:

$$K = \frac{1.98T^2}{L}$$

the liquid to pass through in either direction and is not penetrated by the molecules of the dissolved salt. The cell-wall is *semi-permeable*, and exercises a selective action between the molecules of the solvent and solvend, respectively, in somewhat the same manner that red hot palladium allows hydrogen to pass through it, but not other gases. If such a semi-permeable membrane can be made with perfectly rigid walls, charged with a given saline solution and immersed in pure water, it is only necessary to attach a manometer to determine the force (osmotic pressure) which the water exercises in penetrating the cell and diluting the contents. Pfeffer's artificial cell met the requirements. The porous cup of the ordinary voltaic cell is filled with a dilute solution of copper sulfate, and immersed in a dilute solution potassium ferrocyanid; these meeting within the wall of the cup, form on contact, copper ferrocyanid.¹

When the cell has been prepared, a somewhat difficult matter, a solution of known concentration is placed in it, and it is then hermetically closed with a manometer, and the height of the liquid which equilibrates the osmotic pressure is measured. It

¹ Fouard has made cells by using a metallic web coated with a thin layer of collodion which is impregnated with copper ferrocyanid. By this method it is more easy to determine the proper condition of the membrane than with the porous cell. Such a cell, however, though it has not the rigidity needed to determine the absolute osmotic pressure, serves very well when the problem is to fix, by the zero method, the concentration of typical solution in the outer vessel in equilibrium with a solution in the interior.

is seen at once that this pressure is considerable, and further, that it is proportional to the concentration of the dissolved substance at the absolute temperature. The following figures, obtained from a solution of sucrose, will show the general facts.

1 At the same temperature

Concentration, per cent.	Pressure in mm. mercury	Pressure for unit of concentration
1	535	535
2	1016	508
4	2086	521
6	3075	513

2 At the same concentration:

Temp °C.	Abs temp.	Pressure in mm. mercury	Pressure calcu- lated from the first point by $51 \times DT$
14.2	287 2	510	
15.2	288 2	521	512
32.0	305 0	544	541
36.0	309 0	567	549

Of late, the experiments of Pfeffer have been repeated in England and America with extreme care, and Van't Hoff's conclusions based on earlier investigations have been confirmed. Osmotic pressure of solutions obeys in the same manner as gases,

the laws of Boyle and Mariotte and of Gay Lussac, which can be expressed by the usual equation, viz.

$$pv = p_0v_0\alpha T = RT$$

It is known that the value of R is the same for all gases, on the basis of the gram-molecule, which invariably occupies the space 22,300 cc. (22.3 liters) at 0° and 760 mm. pressure, or 1033 grm. of mercury per sq. cm.

$$R = \frac{1033 \times 22.3}{273} = 84.3$$

With a solution, such as 1 per cent. of sucrose in water, of which the osmotic pressure at 7° is 510 mm. of mercury (693 grm. per sq. cm.) and the volume of one gram-molecule—342 grm. of sucrose—is 34,200 cc. (34.2 liters) the equation will be

$$R = \frac{p^v}{T} = \frac{693 \times 34.2}{273 \times 7} = 84.8$$

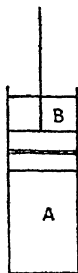


Fig. 13

In other words, the analogy is so complete that the pressure exerted by a gram-molecule of a substance in 22.3 liters of solvent is equal to 1 atmosphere as is the pressure of any gas of which a gram-molecule occupies 22.3 liters.

It can be said further, if a solution A is held (see Fig. 13) under a semi-permeable piston which separates the solution from pure water B , the substance in solution will exercise the pressure that it would exercise if it was entirely gasified in the space which it occupies. Pressure greater than this on the pis-

ton will cause water to pass from A to B, that is will concentrate the solution the same proportion as the volume of any gas in the space would be compressed. Similarly, the solution left undisturbed will expand by absorbing water from B, in the same manner that a gas would expand spontaneously under the influence of the kinetic action of its molecules.¹

MOLECULAR ANOMALIES OF GASES AND SOLUTIONS

Dissociation

Dissociation of Gases.—Some volatile substances have vapor densities not in accord with their molecular weight as determined by their formulas. Phosphoric chlorid, PCl_5 , of which the theoretic vapor density is

$$\frac{208.5}{2} \times 0.0695 = 7.22$$

has a density very much below this, which, moreover, diminishes steadily as the temperature rises. It is not now thought, as was formerly, that this is merely an unexplained exception to Avogadro's postulate, but that the compound suffers partial decomposition on heating, into phosphorous chlorid and

¹ Investigations made by Morse show that to make exact comparison between the osmotic pressure of a solution and the pressure which the dissolved substance would exert if gasified in the given space, it is necessary to consider the volume of the solvent and not that of the solution

The manner in which each molecule of a dissolved substance aids in depressing the freezing point has not been determined; neither has the mechanism of the semi-permeable membrane.

chlorin, which supposition is confirmed by the greenish tint that the vapor exhibits. The higher the temperature the greater the amount of decomposition, and the figure for the density continually approaches to 3.61, which is that of a mixture of PCl_3 and Cl_2 . Reciprocally, by cooling, the chlorin re-unites with the phosphorous chlorid, reproducing the phosphoric form, and at each temperature there is a specific degree of equilibrium between the two conditions and a balance of activity of the reactions so that the action is *reversible*, and is represented thus,



This is an example of dissociation, a general phenomenon, discovered by Henri Sainte Claire Deville.



FIG 14.

In a homogeneous mixture of dissociated gases, the extent, or co-efficient, of dissociation, varying

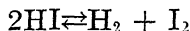
with the temperature, is easily calculated by taking the dissociation of phosphoric chlorid as an example and assuming some temperature. Defining this co-efficient as the ratio of the number of dissociated molecules to those undissociated, we can calculate its value, say at 182° , at which temperature the density of phosphoric chlorid is 5.08 determined by direct experiment. If the initial volume—or the initial number of molecules—of PCl_5 is taken as 1, and α the dissociated fraction,

then the remaining (undissociated) molecules will be $1-a$ and there will have been formed a molecules of PCl_3 and a molecules of Cl_2 . The total mass being the same in both cases, we have

$$\frac{1-a}{1} = \frac{7.22}{5.08} \quad (a = 0.42)$$

that is, of, say, 100 molecules of phosphoric chlorid, 42 have been dissociated and converted into 42 molecules of phosphorous chlorid and 42 of chlorine.

Hydrogen iodid (HI), is dissociated in the same manner by heat; the action can be recognized by the violet tint of the vapor, due to free iodine, but in this case dissociation takes place without change of volume.



The density of the vapor not being modified cannot serve as a datum for determining the co-efficient of dissociation.

Dissociation of Electrolytes in Solution. Cryoscopic anomalies.—Some anomalies similar to those just considered, are met with in cryoscopy, due also to dissociation, but of a particular type and less vividly appreciable in their intimate nature. These abnormalities are generally observed in those substances termed acids, bases and salts. Common salt, NaCl , for instance, always gives by cryoscopy, a molecular weight less than that indicated by the formula (58.5) and the more dilute the solution, the greater is the departure from this figure so that

at the limit it seems as if the molecules were regularly dividing into two groups. With other salts, such as MgCl_2 or K_2SO_4 , the molecule seems to be divided into three parts, while, on the contrary, the molecules of such substances as urea and sugar preserve at all dilutions the normal weight.

These anomalies were discovered in the early application of cryoscopy, and were unexplained until 1884, when a Swedish scientist, Arrhenius, discovered corresponding anomalies in the electrochemical deportment of these salts and laid the foundation of the present theory of *electrolytic dissociation* or *ionization*.

Mechanism of the Transmission of an Electric Current. Ions; Products of Dissociation.—The strict relations established by Faraday's laws (p. 39) between the quantity of current traversing an electrolyte and the quantity of material liberated at the two poles, is a proof that the current passes solely by means of the material that it liberates. The facility of transmission, or *conductivity*, varies with each electrolyte, and even in the same electrolyte, with the concentration of the solution. This conductivity is usually measured by its reciprocal, (the resistance) which is expressed as the resistance offered by a solution between electrodes 1 sq. cm. in area, and separated by an interval of 1 cm.¹ To introduce into the determinations the respective values of the molecular weights of substances being

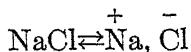
¹For details in regard to these electric measurements, the manuals on electrochemistry should be consulted.

tested, the electrodes are increased in area—without change of distance—so that the volume of liquid includes a gram-molecule of the substance, and in this way the conductivity becomes the *molecular conductivity*.

Water having almost no conducting power, it would be expected that the conductivity of any substance would remain constant at any dilution, but this is not so. 58.5 grm. of sodium chlorid do not show the same conductivity at say such dilutions as 1, 10, 100 or 1000 liters. The conductivity increases with the dilution, although the molecular weight of the salt as determined by cryoscopy decreases with dilution, even reaching half of the 58.5.

These data indicate that the gram-molecule of sodium chlorid dissolved in water gives a number of molecules which tend to be the double of those that would be given by normal volatilization.

The products of these dissociations in solution are termed *ions*, and are the carriers of the current in electrolysis. A moderately concentrated solution of sodium chlorid is made up of some molecules of salt, undissociated, electrically neutral and in equilibrium with ions as indicated in the express on



electrically charged as indicated by the signs. These ions are *not* products of an electric current, and it is this principle that distinguishes the theory of Arrhenius from some that preceded it. The ions exist in the liquid before any electrolysis has

occurred, but as soon as two electrodes carrying a current are introduced into the liquid, the positively charged ions (cations) are drawn to the cathode (negative pole) and deposited or liberated there in succession, losing their electric charge, while the negative ions (anions) travel to the anode (positive pole) and collect there, losing their charge also.¹ The greater the number of ions in a given volume of the liquid, the greater will be the facility of transmission of the current—that is, the lower the resistance—and it will be understood that the conducting power of a sodium chlorid solution will increase with dilution, in other words, with the degree of ionization. Another factor, however, must be taken into account, namely, the mobility of the ions, but this question does not need consideration here. The energy consumed in the passage of the current, is applied to overcoming the resistance offered by the viscosity of the liquid to the transportation of the charged ions towards the respective electrodes.²

What is the exact chemical nature of the ions? Upon this point Arrhenius' theory is not wholly satisfying. It is limited to a view that the charged

¹ It seems to be unfortunate that simple ionization by solution or fusion should be called electrolytic dissociation, as no electrolysis occurs until a current is introduced, as noted in the text.—Tr.

² Like all forms of energy, electricity involves two factors, the quantity of current and the electromotive (pressure) force, and is measured by their product. Faraday's laws concern only the quantity of current; the relations of electromotive force to chemical action are treated of in a later chapter.

ions, Na^+ and Cl^- , for instance, are essentially distinct from free sodium and chlorine, electrically neutral, as we commonly see them. These ions exist in the midst of the water without manifesting themselves by any active reaction or by any color. This difficulty may be left to one side, as the theory of ionization (dissociation) of electrolytes in solution agrees too closely with the data from cryoscopy and from chemical actions to be subject to serious contest. The electrolytes, acids, bases and salts, are just the class of substances of which the cryoscopic molecular weights are abnormal. In fact, in very dilute solutions, as of common salt, the number of free masses, ions or molecules is double that which has been originally dissolved, and each one of these particles, depressing by itself the freezing point, it is clear that for a given weight of the salt, the depression will be double that expected on the assumption of unchanged condition of the salt, and, therefore, the molecular weight will be one-half of that estimated.

Salts such as Na_2SO_4 or MgCl_2 , being dissociated into three ions, in very dilute solutions, *i.e.* 2Na^+ , SO_4^- or Mg^{2+} , Cl_2^- , the apparent molecular weight will be one-third of that which would be calculated from the formulas. On the contrary, non-electrolytes and non-dissociating substances like urea and sucrose, should have and do have, a cryoscopic factor and a normal molecular weight as shown in Fig. 15.

Degree of Dissociation of Electrolytes.—The curves plotted in Fig. 15, show that complete agreement between cryoscopy and conductivity is observed when highly dilute solutions are compared, and

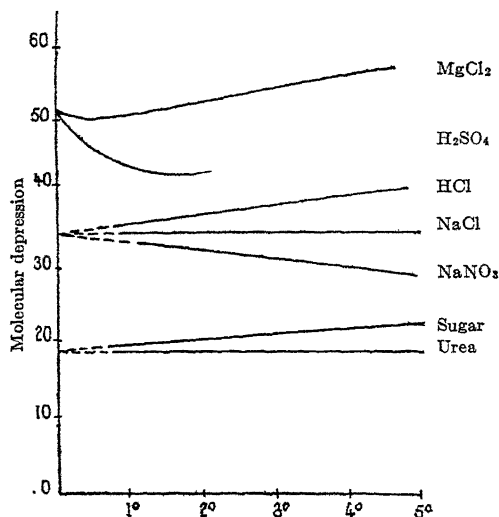


Fig. 15.—Depression of freezing-point of water.

that in moderately concentrated solutions we must expect abnormalities, specific for certain classes of salts, and more accentuated in the sulfates than in the chlorids. Nevertheless, even in dilutions not extreme, the calculation of the dissociation of an electrolyte by both cryoscopy and conductivity will be found to give results in sufficient agreement to constitute proof of the general accuracy of the theory, as the following data show:

By Cryoscopy.—We take as previously, the degree of dissociation as the ratio of the number of dissociated molecules to the total number originally in the amount of substance taken, which is called 1. If each molecule in dissociating produces a number of ions n , there will exist after the dissociation has occurred, a total number of ions and unchanged molecules represented by the expression

$$1 - a + na$$

Calling D^1 the depression of the freezing point of the wholly undissociated substance, that is for the quantity 1 of molecules, and D the depression actually observed, the two data will be proportional to the number of articles that correspond to them

$$\frac{D}{D'} = \frac{1 + a(n - 1)}{1} \text{ from which } a = \frac{D - D'}{D'(n - 1)}$$

D' will be calculated by the equation $D' = K \frac{w}{M}$, which $K = 18.5$. w is the weight of salt dissolved, M the molecular weight corresponding to the formula of the salt, and n the number of ions formed.

By Conductivity.—The molecular conductivity, being for a given substance, proportional to the number of ions, we can write $L = ka$, k being a constant, but at very high dilution at which the dissociation (ionization) is complete:

$$a = 1 \text{ and } L_{\infty} = k, \text{ from which } a = \frac{L}{L_{\infty}}$$

The degree of dissociation is, in this case, determined by the ratio between the molecular concen-

tration of the liquid tested and that which it would have in zero concentration, or in more practical conditions at extreme dilution.

Let us now compare the data from the two methods.

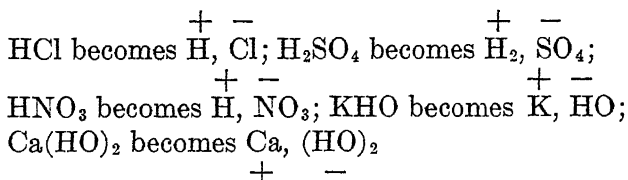
Substance	n	Concentration in gram-molecules per 1000 cc.	A	
			By cry- oscopy	by con- ductivity
Sucrose ($C_{12}H_{22}O_{11}$) . . .	0	0 3	0 08	0 0
KCl.....	2	0 14	0 93	0 86
LiCl	2	0 13	0 94	0 84
MgCl ₂	3	0 38	0 20	0 35
Ca(NO ₃) ₂	3	0 18	0 73	0 73
SrCl ₂	3	0 18	0 76	0 75

The agreement is only approximate, but it is fairly satisfactory if we take into account certain secondary reactions that may interfere. For instance, it is known that in solutions of magnesium sulfate some of the non-ionized molecules unite in pairs, which, of course to some extent cancels the effect of the dissociation of other molecules.

Dissociation and the Reactions of Substances in Solution.—The theory of ionization serves not only as an explanation of the movement of a current through a liquid, but has wide application in chemistry, if we accept Arrhenius view that the reactions of dissolved substances affect only those molecules that are dissociated. Some general and

important instances of the application of this view may be here cited.

All acids are characterized by some common properties, among which are power to change organic colors and to cause effervescence with carbonates. It is logical to ascribe these properties to some constituent common to all. This constituent is ionizable hydrogen. Similarly, the compounds collectively known as bases, exhibit common properties, which are naturally ascribable to a common constituent, in this case hydroxyl (HO). The dissociations in the two classes are illustrated by the following formula



In moderate dilution some of these substances may undergo less complete ionization. Thus, sulfuric acid may be converted into H, HSO₄. It is evident, that the activity of an acid or a base will depend largely on the extent to which it ionizes under given conditions. The molecular conductivity of these substances therefore will be greater in proportion as the dissociation increases. Now, experiment shows that hydrochloric acid has a much greater conductibility at a given dilution, than acetic acid at the same dilution. There is, therefore, in the case of the former a much higher dissociation,

and in the same manner sodium hydroxid solution is a much better conductor than ammonium hydroxid, which latter is in its chemical relations much the feebler. The annexed table gives a view of some of these comparisons.

Concentration in gram-molecules in 1000 c. c.	Equivalent conductivities, i.e. conductivities of solutions containing 1 gram-equivalent of each substance in solution, electrodes 1 cm. distant* (acetic acid)			
	HCl	HC ₂ H ₃ O ₂	NaOH	NH ₄ OH
1 0	301	1.32	157 0	0 89
0.1	351	4 6	195 4	3 3
0.01	370	14.0	203.4	9 6
0.001	377	41 0	204.6	28 0

* The gram-equivalent of an acid is the weight of this acid that will exactly saturate the unit of base, say a gram-molecule of sodium hydroxide. With monobasic acids, as HCl, it is the same as the gram-molecule; with dibasic acids, as H₂SO₄, it is one-half, and with tribasic acids, as H₃PO₄, it is one-third.

Thus, the chemical activity, commonly called the *power or avidity* of the acids, increases in the same way as the equivalent conductivity, one being a measure of the other. (See Appendix B).

The extensive dissociation of powerful acids and bases is in accord with the fact that the quantity of heat liberated in their respective interactions is the same.¹

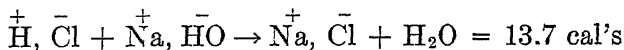
¹ This is true only for acids and bases in solution; the heats of neutralization in the solid state are quite different, even with strong acids and bases. Works on Thermochemistry may be consulted for more detailed information.

One gram-molecule of sodium hydroxid saturating 1 gram-molecule of

HCl	disengages 13 7 calories
HBr	disengages 13 7 calories
HI	disengages 13 7 calories
HNO ₃	disengages 13 7 calories
HIO ₃	disengages 13 8 calories

Two gram-molecules of sodium hydroxid in solution disengage 27.2 (13.6×2) calories in saturating 1 gram-molecule of chloroplatinic acid, H_2PtCl_6 .

In fact, in very dilute solutions to which these thermochemical data apply, the strong acids, bases and their salts are practically completely dissociated. The ions are free after as before neutralization, except as to H and HO, which combine, producing water which is but slightly ionized under any condition.¹ The following equation illustrates the general character of these reactions.



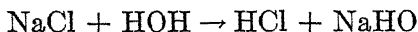
The disengagement of heat in cases of the same type is uniform, because it corresponds to constant phenomenon of combination, that of H and HO.

To sum up, the theory of dissociation brings into harmonious relations so many diverse phenomena that it cannot be considered other than a physical truth. Its weak point is the precise definition of the ion itself inasmuch as we, at present, do not

¹ Water very highly purified is a very poor conductor of electricity, and evidently contains a very small amount of ionized molecules. For a discussion of this subject and some important applications, see Appendix B.

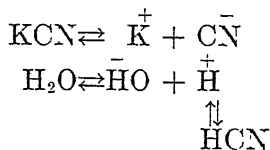
understand the manner of its formation, nor its chemical nature. How can the simple action of solution break apart two constituents of such high chemical affinity as Na and Cl in common salt, the separation of which seems to require a high consumption of energy? It is difficult to conceive the part taken by the water in a phenomenon which passes within its structure and which is the stronger in proportion as the amount of water is greater. No satisfactory response has yet been given to these objections.

Hydrolysis.—Attempts have been made, it is true, to show that the elements of water enter into the act of ionization, but this view has not, so far, received much approval. The most simple of the modifications proposed consists in supposing that a neutral salt is dissociated into an acid and a base, within the immediate mass of water, thus,

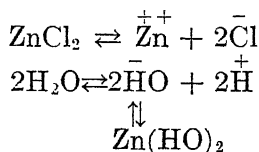


but such a view seems applicable only to salts, the acids and bases from which are feeble, and not to neutral salts. This type of reaction is indeed well known under the name of "hydrolysis," and is manifested by the development of either an acid or an alkaline reaction in the solution. The ionization theory, under its ordinary form, interprets the action somewhat crudely, but logically, by ascribing the reaction of the water to self-ionization, which can become quite effective if the ions H and HO respectively, disappear as they are formed.

For instance, potassium cyanid, KCN, a salt derived from a feeble acid and strong base is hydrolysed, because hydrogen cyanid (hydrocyanic acid) is very slightly dissociated, the H ions being held in great part by the CN ions:



The HO ions are also in equilibrium with the K ions, but they are present in high proportion, potassium hydroxid being a base of high dissociating power, hence the marked alkalinity of the solution. Reciprocally, zinc chlorid has a strong acid reaction in solution, because it is derived from a strong acid and a weak base, which latter is but little dissociated,



These instances, however, relate to certain types of substances, salts with acid or alkaline reaction. With neutral salts, the action of water is indicated not by hydrolysis but by dissociation, and the chemical formula of this type of action is still to be ascertained. Undoubtedly, it will be necessary to take into account the molecular complexity of water, which, in its liquid state, is a mixture of

several types of equilibrium, two, at least, *i.e.*, H_2O and $(\text{H}_2\text{O})_2$ and possibly a third $(\text{H}_2\text{O})_3$, though the existence of the last is less sure.

CONCENTRATED, SATURATED AND SUPERSATURATED SOLUTIONS

Curves of Solubility and Supersolubility. Existence of Hydrates in Solution. Is Solubility a Function of the Dimensions of the Crystals?

When a solid is put in contact with a solvent, and shaken for some time until no more dissolves, the limit of solubility, saturation, is attained which is subject to variations with the temperature, which variations can be represented by curves of solubility. Usually the temperatures are scaled as the abscissas, and the saturation concentrations as the ordinates, the latter expressed in grams of the anhydrous substance in 100 grm. of water, each point being determined by test of a weighed sample of the solution saturated at a given temperature.

The forms of the curve here shown in Fig. 16 for some of the salts of the alkali-metals are quite diverse, almost straight in the case of chlorids, very strongly curved for the nitrates and chlorates. The curve of sodium sulfate, which is one of those most carefully studied, presents some peculiarities of special relation to all saline hydrates, and even salts in general. (See Fig. 17.)

The diagram shows as many curves as there are different forms of the salt, the anhydrous salt and the several hydrates having each a specific solu-

bility. At the point E_2 the ordinary commercial salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) co-exists in equilibrium with the anhydrous form and at the same time with a

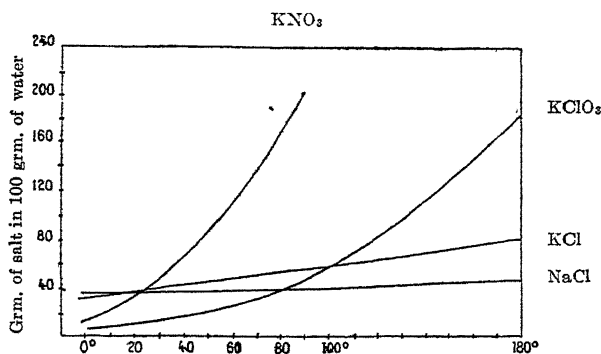


FIG. 16.—Curves of solubility.

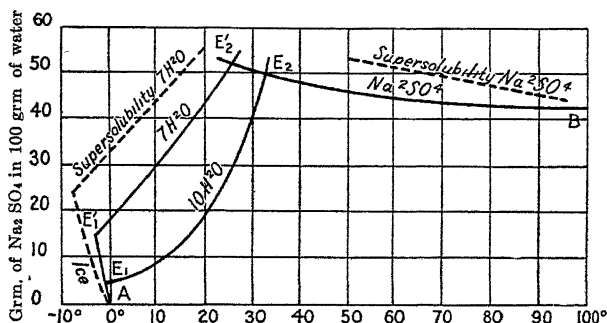


FIG. 17.

saturated solution of the two forms. E_2 is a fixed point, corresponding to a temperature 32.48° which can serve as datum in thermometry; it can

be attained very easily by heating gently the decahydrated salt ($\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$), which will melt in its water of crystallization at 32.48° . Beyond this point sodium sulfate is always anhydrous.¹

The point E_1 , another point of retrogression, corresponding to a transformation, is the point of equilibrium between ice, the decahydrate and the saturated solution; it is not possible to maintain the others at the point of stability of the solid decahydrate, its saturated solution and ice, except at a temperature corresponding to E_1 say, -1.2° . At the temperatures and concentrations that correspond to E_1A , only ice is formed, and in conformity with the law of cryoscopy, determining the proportionality between the concentration and the depression of the freezing point of a dilute solution, this portion of the curve is perfectly rectilinear in the neighborhood of A.

Supersaturation.—The curve E'_1, E'_2 corresponds to the deposition of a somewhat unusual hydrate, $\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$, which is produced when hot saturated solutions of sodium sulfate are allowed to cool in a tightly closed flask. The solubility of this (hepta) hydrate at a given temperature being greater than that of the deca-form ($10\text{H}_2\text{O}$), a saturated solution of the former is supersaturated and unstable with relation to the latter. Such a

¹ Consequently, when anhydrous sodium sulfate is employed to dehydrate organic liquids, by the formation of the decahydrate, the operation should not be carried out above 32.5° .

solution exposed to an atmosphere free from suspended particles, as by filtration through a wad of cotton, will deposit the heptahydrate, but on contact with even a minute fragment of the decahydrate, this salt being less soluble will separate at once. (This is commonly termed crystallization by inoculation). Such a crystallization happens commonly when the solution is exposed to the air, due to the presence of minute crystals of the decahydrated sodium sulfate in the air dust.

Solubility Curves.—On the other hand, even in the absence of crystalline particles, a supersaturated solution of sodium sulfate cooled to a sufficiently low temperature—the particular point depends on the degree of supersaturation—, will crystallize spontaneously, especially if shaken.

To distinguish these two degrees of instability in supersaturation, Ostwald proposed to apply the term “metastable” to the condition in which crystallization is produced by inoculation, and the term “labile” to those solutions that crystallize without inoculation, *i.e.*, spontaneously. The distinction is not simply one of terms, for the experiments of H. A. Miers and his associates enable us to fix the limit of the two conditions and represent it by curves of *supersolubility*, curves that are determined by the temperatures at which the supersaturated solutions of known strength crystallize spontaneously.

The curves of supersolubility of sodium sulfate plotted in Fig. 17, have been constructed by

Hartley, Jones and Hutchinson, using the following procedure.

Known weights of water and the decahydrated salt ($\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$) are sealed in glass tubes into which fragments of glass or platinum have also been placed, intended to bring about crystallization by friction on the walls of the tubes. The tubes are heated until the salt dissolves completely, then cooled with continual agitation in a bath the temperature of which steadily decreases, this temperature being watched carefully and the point noted at which crystallization begins. As the results of this method are subject to some irregularities, several experiments should be made and the average taken. This datum, taken in connection with the known concentration of the solution, defines a point on the supersolubility curve (Fig. 17). It is evident by the breaks in the curve, as well as by the appearance of the crystalline mass, that the curve of supersolubility of sodium sulfate is made up of several sections, corresponding to the several forms of salt deposited, as is the case with the curve of ordinary solubility.

Below the ratio of 25 parts of sodium sulfate to 100 of water, a supersaturated solution deposits ice in spontaneous crystallization; above this percentage, the heptahydrate is deposited, without any need for cooling to a low point, because, as shown in Fig. 17, a 50 per cent. solution deposits spontaneously the heptahydrate at about 15° .

Finally, the supersolubility anhydrous sodium

sulfate diminishes in proportion as the temperature rises, as does the solubility of the same, in such a way that the said 50 per cent. solution which yields the heptahydrate near 15° , gives spontaneously a deposit of the anhydrous salt when heated to about 60° .

On the other hand, it is impossible to plot a curve of the supersolubility of the decahydrate, because this form, the usual product of crystallization of sodium sulfate in contact with air, is separated only rarely from supersaturated solutions, and under conditions so irregular as to prevent the determination of a definite line.

Ordinarily, the supersolubility is shown in the common solutions crystallizing in contact with air, by the separation in succession of two deposits, that can sometimes be distinguished by careful scrutiny. The first crystals are formed when the temperature and the concentration are at the point of saturation of the solution; then in proportion as the mass cools, the excess of dissolved substance is slowly separated, the solution, however, remaining supersaturated, and it is only after cooling several degrees further that suddenly a second separation, more abundant than the first occurs. The first deposit corresponds to the solubility at a temperature t ; the second to a supersolubility at a temperature t' , below t . The phenomenon of crystallization by two stages has been summarized by Miers in the following manner.

The curves of solubility and supersolubility of a

salt being given, the lines $ABCD$ and ABE represent the state of a solution about to crystallize in contact with the air. At A it reaches the point of saturation, without crystallizing, then the temperature falling and an inoculation particle entering the solution, crystallization commences. If the fall in

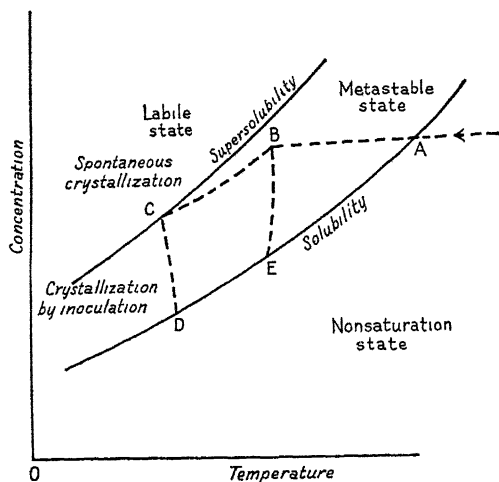


FIG 18.

temperature is rapid, the line BC , which represents the variations of temperature and concentration of the solution, reaches in C the curve of supersolubility, then, promptly, a rapid and abundant crystallization occurring, the solution is depleted to a point of stability, D , appertaining to the curve of solubility, as determined by the temperature conditions.

If, on the contrary, the cooling is slow, the first deposit appearing at *B*, influences steadily the crystallization of the excess of the salt, and the condition becomes finally that indicated by *E*, without the solution reaching a state of supersolubility.

Existence of Hydrates in Solution.—These phenomena of solubility and supersolubility are evidently dependent on the state in which a salt exists when in solution, about which but little is

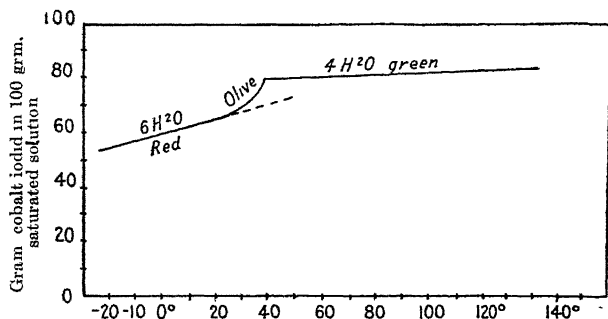


FIG. 19.

known. In concentrated solutions, dissociation is slight, and the electrically neutral molecules are in great majority, but are these molecules in a true anhydrous conditions or in the form of definite hydrates, as numerous as the departures in the curves of solubility, and are the hydrates of the same composition as the ordinary crystallized forms of the given salt? The tendency of opinion is to the second view, and it receives support in one case indicated by Etard. Cobaltous iodide, CoI_2 , forms two hydrates, with 4 and 6 molecules of water

respectively, of which the curves of solubility accord about 40° . The $4\text{H}_2\text{O}$ crystals are red; those with $6\text{H}_2\text{O}$, green. Now the saturated solution of the salt is red below 40° and green above that point; seems, therefore, that at the respective temperatures the salt is associated with the proportion of water that is found in the crystals of corresponding color.

Is Solubility Influenced by the Dimensions of the Crystals?—It seems probable from some observations of Ostwald, that the solubility of a definitely crystalline substance may be influenced by the size of the crystals. For instance, the mineral gypsum, $\text{CaSO}_4, 2\text{H}_2\text{O}$, in ordinary powdered form dissolves in water to the extent of 2.08 grams in 1000 cc. at 25° , but if to such a saturated solution we add a little gypsum in extremely fine powder, some will pass into solution and the concentration will rise to about 2.4 gm. to 1000 cc., but will later return to the original strength. This phenomenon is explicable upon theory that extreme powdering transforms the crystalline state to the amorphous, and it is not necessary to assume a variability in the coefficient of solubility.¹ The amorphous condition of any substance is always less stable and more soluble than the crystalline, hence the addition of the extremely fine powder raises the solubility until the moment when the added mass returns to the crystalline, more stable and less soluble form.

¹ Changes of this character have been noted in cry tallography and metallography.

SOLID SOLUTIONS

What has been considered in the preceding sections relates to the most important type of solution, that of solids in liquids and especially in water. Solution, however, is a much more general phenomenon. Gases dissolve in liquids, as in the well known instance of air in water; gases dissolve in solids, as in the case of hydrogen in palladium.

Liquids are frequently soluble in each other, in some cases, as with alcohol and water in any proportion, often in definite ratios, governed by temperature. Thus, if ether and water are shaken together for a time and then allowed to rest, two layers will be formed. At 0° the lower watery layer consists of 15 grm. of ether to 100 grm. of water, and the upper ethereal one consists almost entirely of ether, only 2 grm. of water to 100 per cent. of ether being present. At 60° , the ratio of solubilities will be, in the lower layer, 3 grm. of ether to 100 grm. of water, and in the upper layer 3 grm. of ether to 100 of water.

Lastly, solids can form with each other homogeneous mixtures, in which some of the characteristic properties of solutions are exhibited. Among these characteristics are: miscibility in different proportions, existence of limits of solubility, capacity of diffusion. For these associations, Lecoq de Boisbaudran and later Van't Hoff proposed the name *solid solutions*. A remarkable instance of inter-diffusion of solids is the association of gold and lead as observed by Roberts-Austen. Gold

leaf applied firmly to the base of a cylinder of lead, diffuses slowly into the mass of the latter, and can after a time be found in appreciable amount. From the content of gold at a given point from the base, and the record of the time during which the action has been going on, it is possible to calculate the rate of diffusion. It is extremely slow at ordinary temperatures, but actual, because at the end of 4 years gold was detected at a distance of 7 mm. from the base of the lead cylinder. In accordance with the general theory of molecular motion (kinetic theory) the diffusion is accelerated with the increase of temperature, and the following figures are derived from experiment.

Amount, in grams, of gold diffusing in one second for 1 sq. cm.

100°	0.0023×10^{-7}
165°	$0.46 . \times 10^{-7}$
200°	$0.8 . \times 10^{-7}$
250°	$3.5 . \times 10^{-7}$

Glass is a solid solution, being amorphous mixtures of different chemical compounds, which have passed from a complete fluidity at a high temperature, insensibly, to an extreme viscosity when cold, without showing any definite point of solidification.

Mixed crystals of isomorphous substances have analogies to solid solutions, inasmuch as they are homogeneous, and are variable in composition, but they are distinguished by orientation of properties, which is so characteristic of crystalline structure,

while solutions exhibit the same physical and chemical properties in all directions. With non-isomorphous solids there is often not a trace of miscibility, as is exhibited in the natural rocks, in which distinct crystalline species co-exist although they have been in contact for long periods.*

DIAGRAMS OF FUSIBILITY

In the study of mixtures of salts, and especially in the study of alloys, use is made of diagrams of fusibility, of similar principle to those used in plotting the curves of solubility of substances in water, but of somewhat different aspect. Take, for example, potassium nitrate, the solubility of which in water increases rapidly with the rise of temperature. The content of water in the saturated liquid is much diminished, and soon a fused condition is reached, at which the salt takes a liquid condition without addition of water, and this marks the upper limit of the curve of solubility. Reciprocally, the curve of solubility, after having passed the *eutectic* point, finds its lower limit at the point of fusion of the solvent. A curve of solubility, therefore, taken in its entirety, is the curve of fusibility of a system of two components, water and the salt.

On the other hand, it is usual to plot diagrams of fusibility so that the ordinates carry the temperatures and the abscissas the concentrations. Moreover, the concentrations are expressed in per cent. by weight of the total mass, while in plotting solu-

bility curves it is still customary to express the concentration in relation to the weights of the two components, which has the disadvantage of involving an infinite ordinate at the fusing point of the dissolved substance.

The Case of Two Components Not Isomorphous.—Take the case of antimony and lead. To plot the diagram of fusibility, a number of alloys are pre-

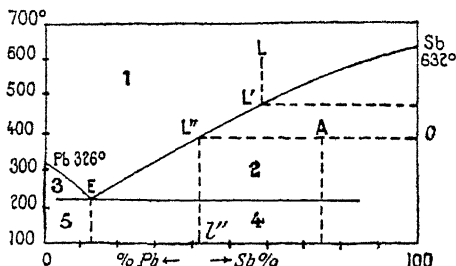


FIG. 20

pared containing known proportions of the two metals, each is tested to determine the temperature at which it begins to solidify. The weight relations being noted on the abscissa, the point of beginning solidification on the ordinate, two curves will be developed, which will intersect at the eutectic point, *E*, as 228° and 87 per cent. of lead.

At this eutectic point we know that the whole mass of the alloy has solidified to a heterogeneous mixture of the two constituents but very thoroughly intermingled, and that the temperature remains constant from the beginning until the end of the solidification. This does not occur with non-eutectic

mixtures, for in these the solidification is made in two periods. The best method to determine these points is to measure the rate of cooling of the mixture, noting at regular intervals the temperature indicated by a thermoelectric couple immersed in the molten mass, protected by a refractory sheath. As long as the mass is homogeneous and fluid, the speed of cooling follows the path AB , but at B , pure

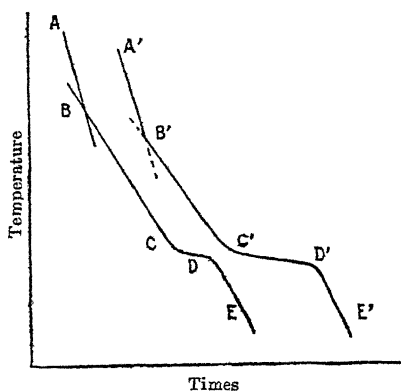


FIG. 21.

antimony, or pure lead separates, according to whether the composition of the mass lies to right or left of the eutectic, and the speed of cooling slackens. The point B , which it would be quite difficult to fix by means of the pyrometer, is sharply indicated graphically by the intersection of AB with CD . Later, the alloy, depleting itself more and more of the constituent that is solidifying, is reaching

steadily the eutectic composition, and finally solidifies as a whole, at a fixed point along the line of the horizontal D ; when the mass has become solid throughout, the cooling again becomes more rapid, since it is no longer retarded by the disengagement of heat from the change of state.

In the diagram, Fig. 20, a mixture having its characteristic at F is entirely melted; by cooling, the

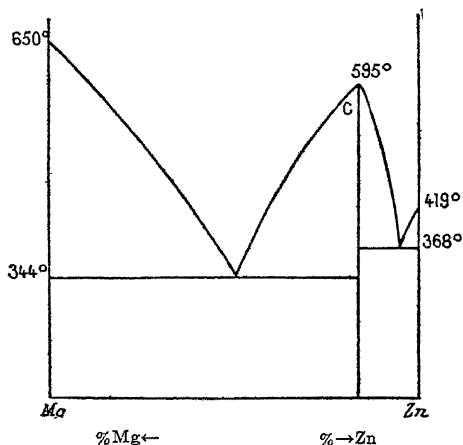


FIG. 22.

point passes to L' , the homogeneous fluid mass separates into two portions, one solid, of pure antimony, the other liquid. The solid mass increases without change of composition, while the liquid continually changes until it reaches the abscissa E . On the other hand, if we test a mixture of the two metals having the characteristic at A , its physical state is indicated on the diagram by the horizontal

line $L''A\theta$, the mixture is divided at the given temperature into pure, solid antimony, and a liquid of the composition l'' . As a whole, the diagram exhibits five areas. 1, complete fusion; 2, equilibrium between pure, solid antimony and fused mixtures of lead and antimony containing from 0 to 87 per cent. of the former metal; 3, equilibrium between pure, solid lead and liquid mixtures of lead and antimony containing from 0 to 13 per cent. of the latter; 4 and 5, completely solid mixtures of eutectic alloy and pure antimony for area 4, and the eutectic alloy and pure lead in 5.

Case of Two Components, Not Isomorphous, but Forming a Definite Combination.—If a definite combination, C , is formed between the two components A and B , the diagram of fusibility will be composed of two juxtaposed diagrams, each having its eutectic and meeting at the point of fusibility of C . Fig. 22 shows the phenomena of a zinc-magnesium alloy ($MgZn_2$) and indicates that the point C has for the abscissa, the definite composition as indicated in the formula and for the ordinate the melting point of it. It is thus possible to determine the existence of a combination, its formula, its melting point and the limits of its formation, without isolating it, this last a task indeed, sometimes impossible. In this manner is established a method of thermic analysis based on differences in fusing points as functions of composition. If several combinations are formed, each one is marked by a maximum in the curve; such is the case with water and sulfuric anhydrid, as shown

in Fig. 23, which is a diagram of the remarkable succession of hydrates of sulfuric acid.

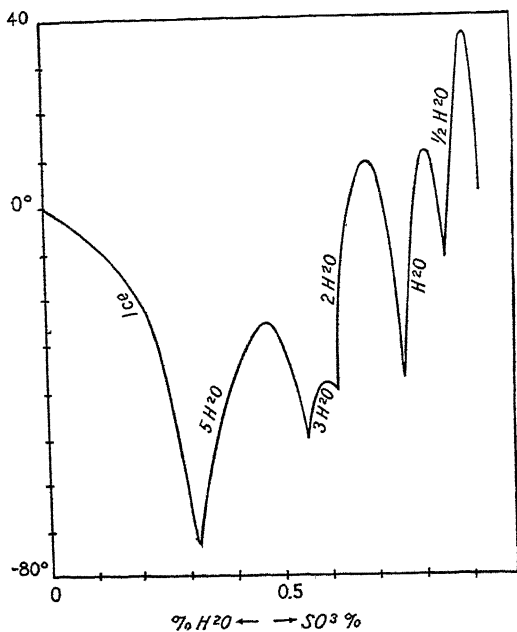


FIG 23.

Case of Two Isomorphous Components.—The phenomena just described are exactly comparable to those which are exhibited in the crystallization of watery solutions. Each component of the system depresses the melting point of the other, and the two curves intersect at the corresponding eutectic, this being, in the case of water, ice on the one part and a definite hydrate of the salt in solution on the

other part. If we dissolve two isomorphous salts, for instance, common alum and chrome alum, the composition of the mass that crystallizes is variable, as is also the mother liquor, and the two portions are not alike. Analogous cases are found in many alloys, for instance, in those of copper and nickel. The curve shown in Fig. 24 has been con-

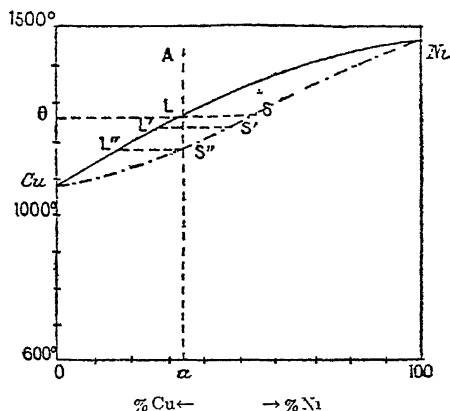


FIG. 24

structed by determining at several temperatures, the composition of the liquid portion (L), and the solid portion (S) of such an alloy of known composition and in process of solidification. It shows that if this alloy in perfect fusion, as represented by the point A , is allowed to cool to the temperature θ , a solid alloy separates having the composition corresponding to the abscissa S while the liquid has a composition corresponding to L . As the cooling proceeds, the fluid portion becomes richer in copper,

the more fusible of the two metals, and its characteristic point follows the curve LL' . If the cooling is quite slow and the diffusion within the fluid mass active, so that the alloy S maintains a condition of equilibrium with the liquid portion, its composition will become S' . As the cooling proceeds, the volume of the solid increases steadily, and that of the liquid diminishes 'until it becomes zero at S'' , at which the alloy returns to the condition of homogeneous solid having the initial composition a . In practice, however, diagrams of fusibility are rarely so simple as the one shown.

Many isomorphous substances are miscible only in definite limits; this fact has been long known from researches in crystallography. Thus, monoclinic ammonium chromate and orthorhombic ammonium sulfate crystallize with each other in proportions that range from 0 to 56 per cent. of the latter to the former and also in proportions from 86 per cent. to 100 per cent. Crystals obtained in the first series of proportions, *i.e.*, up to 56 per cent., are predominantly orthorhombic; crystals containing the higher ratios are monoclinic. In the proportions of 57 per cent. to 85 per cent., intermediate between the two other proportions, neither salt is in sufficient excess in the solution to impress its form upon the other and they form independent crystals, each in its form. Such substances are termed *isodimorphous*.

The peculiarities appear in the structure of alloys as well as salts, and when isomorphism or isodimorphism is concerned in systems in which definite com-

pounds arise, the diagrams of fusibility become very complex, for examples of which works on thermic analysis should be consulted.

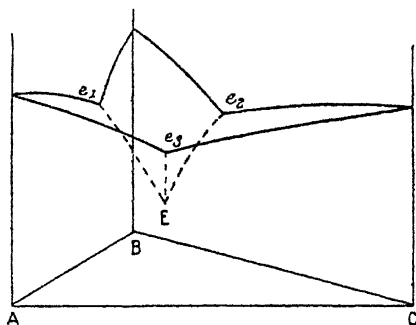


FIG. 25.

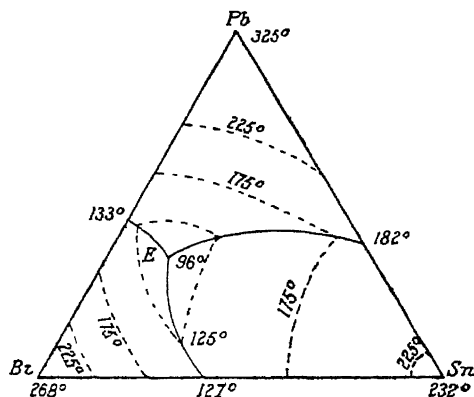


FIG. 26

Case of Three Components Not Isomorphous.—In this class consideration will be given only to ternary mixtures, and merely to illustrate their graphic rep-

resentation, in a simple example, that of fusible alloys of the Darcet type, and especially the lead-tin-bismuth alloy studied by Charpy.

The system of co-ordinates consists of a triangular prism, with an equilateral base. The sum of the distances of a point in the triangle from its three sides being constant and equal to the height, is taken as 100; every point in the base represents in hundredths the composition of the ternary mixture, and the vertical at this point expresses the temperature of initial solidification. Each face of the prism represents the diagram of fusibility of the components, taken in couples, and the three binary eutectics find agreement in the ternary eutectic point *E*.

Finally, we can simplify the construction by projecting it on its base and inscribing the temperature on the curves as shown, which are the projections of the curves of equal temperature obtained by cutting the surfaces represented in Fig. 25 by horizontal planes.

CHAPTER VI

CHEMICAL AFFINITY

Observation of the phenomena of active combination long ago suggested that a special attraction or affinity exists which influences substances placed in contact, and that this affinity may be measured by the heat disengaged in the action. This measurement is the object of *thermochemistry*. The heat disengagement is the resultant of the transformation of the latent chemical energy of the reacting substances into heat. It is accompanied by a degradation of chemical energy, but does not give an exact measurement of this degradation. If a reaction can be brought about which gives the same products by the mechanism of a reversible cell, then the energy set free by the action takes the form of electric energy, and if the two amounts thereof and their respective factors (chemical affinity, electromotive force) are compared the chemical force can be measured by the electric force. Here then is another method more precise, but of limited application for determining the relative magnitude of affinity.

Finally, the speed of a reaction is a direct function of affinity, but is a complex problem and not

always accurately measurable. It will, however, be considered first, not so much for its direct value, but as a preface to a study of the laws of chemical action.

SPEED OF REACTION

Chemical reactions are accomplished at widely different rates of speed. Some seem instantaneous, as the action of acids and bases and that of chlorine and hydrogen; others are comparatively slow, such as the etherification of an alcohol by an acid, the inversion of sucrose, the combination of sulfur and hydrogen. The latter types are alone measurable, but they are subject to several factors of uncertainty. For example, when the portions of the same acid are put in contact with a series of metals with which it reacts, the volume of hydrogen evolved in a given time is a rude indication of the relative affinity of the metals tested, but the actions depend also upon the temperature, the extent of surface of the piece of metal used, the concentration of the acid, and its impurities. It is assumed that the samples of metal used are very pure, for a small amount of impurities in some metals materially affects their activity. Hence, a grading of the affinity of a series of metals cannot be made without strict attention to many details. The speed of a reaction depends therefore on many accessory factors as well as on the affinities of the reacting substances.

INFLUENCE OF CONCENTRATION ON THE SPEED OF REACTION

Reactions are classed as mono-, bi-, etc. molecular, according to the number of molecules involved.

Monomolecular Reactions.—The decomposition of hydrogen arsenid by heat, studied by Van't Hoff, affords an excellent means of determining reaction-speed, as it is not reversible, that is, not counter-balanced by an opposing action.



At 310°, the temperature always chosen, the arsenic deposits as a solid, and does not re-unite with the hydrogen. It is evident that the concentration of the hydrogen arsenid steadily diminishes, but the question is what amount in a given time. The simple view, and one that is sustained by experiment, is that the decomposition of any particular molecule concerns only the molecule itself, and that, in a given brief time, the number of molecules decomposed in a unit volume is proportional to the total number of molecules in that volume. Therefore, calling k a constant factor, C the concentration, that is, the number of molecules in the given volume, t the time, and v the speed of the reaction, that is, the diminution of the number of gram-molecules in 1000 cc. in a unit of time, then, if at the initial time,

$$C = C_0$$

then

$$(2) \quad \text{Log } \frac{C}{C_0} = kt$$

In order to introduce a magnitude more directly measurable than the volume of a gas, the concentration is replaced by the pressure, and the problem is changed as follows:

If, at the beginning of the change, n molecules of the substance existed in 1000 cc., and if at the end of the time, t , n' molecules have been destroyed, the total volume of the gas being maintained constant during the experiment, by a steady and suitable increase of pressure, the corresponding concentrations of the arsenid are

$$\frac{C_0}{C} = \frac{n}{n - n'}$$

now n molecules of AsH_3 produce $\frac{3}{2}$ molecules of H_2 ; the pressures at the respective times, initial, designated by P_0 , and at time t , by Pt , will be as the respective molecules present, say

$$\frac{P_0}{P} = \frac{n}{n - n' + \frac{3n'}{2}}$$

from which

$$\frac{C_0}{C} = \frac{P_0}{3P_0 - 2P}$$

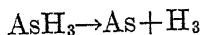
and according to (2)

$$k = \frac{1}{t} \log \frac{P_0}{3P_0 - 2P}$$

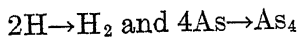
Van't Hoff obtained the following data by experiment:

t in hours	Pt in mm. of mercury	k
0	784 8	
3	878 5	0 0908
4	904 0	0 0905
5	928 0	0 0980
6	949 3	0 0905

The agreement in the value of k indicates the validity of the theory; the speed of decomposition at each instant is proportional to the molecular concentration of gas at the same instant. This simple result raises, however, one problem in the use of symbols, for to show exactly the function of the whole molecule, we ought to write the equation $2\text{AsH}_3 \rightarrow \text{As}_2 + 3\text{H}_2$ or better $4\text{AsH}_3 \rightarrow \text{As}_4 + 6\text{H}_2$ inasmuch as arsenic is tetratomic. The joint action of 2 or 4 molecules being necessary, the reaction is strictly bimolecular or tetramolecular, with a speed, as will be seen later, proportional to the square or to the fourth power of the concentration, which is contrary to the observed data. To explain this inconsistency, Van't Hoff has ingeniously suggested that the decomposition proper is monomolecular



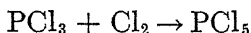
but that this change, slow and primary, is followed by two secondary changes by condensation, thus



which are so rapid that they do not affect the quantitative relations of the primary action. The determination of the speed will give, therefore some insight into the mechanism of the reaction.

Van't Hoff has pointed out that the speed of decomposition of hydrogen arsenid is low, and that it can be inferred that all the molecules of the gas are not in the same state at the same moment, otherwise they should decompose all at once or not at all. But it is probably just as rational to assume that the decomposition is propagated under the influence of some impurity acting as a catalyst (see p. 150). It is known that certain impurities are essential to some types of combinations and decompositions. Vapor of water is among these determining agents. It seems probable that a catalytic agent can act only on a limited number of molecules in a given time, and in this light we can understand that only a limited number of molecules can be influenced in the unit time.

Polymolecular Reactions.—When two or more molecules take part in a reaction, we can infer, with some confidence, the relation between the speed and the molecular concentration, by considering, as a simple instance, the case of a gas, and associating in the action a kinetic feature. To show this, take the reaction

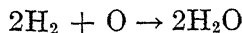


at a temperature at which all three are gases. The union of chlorine and phosphorous chlorid can be

brought about only so far as there is contact and collision between the several molecules. The number of collisions being proportional to the molecular concentration, (C), the reaction-speed will also be proportional to said concentration of each substance, and will be the product of these factors. Therefore, we have

$$v = k C_{Cl_2} C_{PCl_3}$$

Further, if two molecules of the same type take part in the reaction, as in the formation of water,



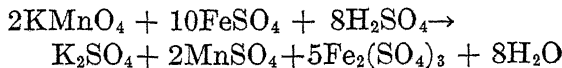
Their concentration will be expressed by the square in the equation of speed, thus

$$v = k C_{H_2}^2 C_{O_2}$$

In general, if a reaction involves molecules $nA + n'A' + n''A''$, its speed will be expressed by

$$(1) v = k C_A^{(n)} C_{A'}^{(n')} C_{A''}^{(n'')}$$

In actual experience, n' , n' , n'' are never large. nor are the different substances A, A', A'' numerous, since, up to the present time, very few reactions are observed in which it is necessary to express in the equations thereof more than two or three types of molecules. Thus, when we state the reaction between ferrous sulfate and potassium permanganate, under the usual form



we merely give the final result of a series of molecular reactions each in itself simple. From the point of view of the kinetic theory, it is probable that complicated reactions are exceptional, since the more numerous the constituents of a given molecule, the less is the chance of their encountering each other at the same time and place. In spite, however, of the reasonableness of the kinetic view, it must be considered only as a suggestion, and not as a full demonstration of equation (1) p. 125. The number of molecular collisions, is indeed, a factor of reactions, but not a preponderating one, as is proved by the fact that the speed of a reaction may be increased two or three times by an increase of 10° in temperature, while the number of collisions deduced from the principles of the kinetic theory, is increased only in proportion to the square root of the absolute temperature, perhaps 1100 or 1200 in the same temperature interval.

Homogeneous Chemical Equilibrium. Law of Mass Action.—The decomposition of hydrogen arsenid, just studied, is an irreversible reaction, but many other decompositions, such as that of phosphoric chlorid (PCl_5) are counterbalanced by an inverse action of combination,



and when equilibrium is established, we can say there is formed in a given time as much phosphoric chloride as is decomposed, so that

$$v = v' \text{ or } kC_{\text{Cl}_2} C_{\text{PCl}_3} = k' C_{\text{PCl}_5}$$

from which

$$(1) \quad \frac{C_{\text{Cl}_2} C_{\text{PCl}_3}}{C_{\text{PCl}_5}} = \frac{k'}{k} = K$$

K is a constant at a given temperature.

This is an expression of the law of *mass action*, a law of which Berthelot was the initiator, inasmuch as he introduced into chemistry, the idea that the result of a reaction depends not solely on the nature of the substances concerned, but also on their amounts, that is, an excess of one of the reacting substances may compensate for the low degree of its affinity.

An illustration of the operation of this law is found in an experiment first performed by Berthelot and Péan de Saint-Gilles, in 1862 and often repeated since.

Acetic acid and ethyl alcohol react to form water and ethyl acetate, inversely these two substances, mixed in a pure state reproduce acetic acid and ethyl alcohol $\text{HC}_2\text{H}_3\text{O}_2 + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}$

$$(2) \quad K = \frac{C_{\text{ether}} C_{\text{water}}}{C_{\text{acid}} C_{\text{alcohol}}}$$

It is now proposed to show that the value of K , which results from the measure of the molecular concentrations is equal to the relations between the speed-constants k and k' observed separately at the beginning of each of the opposing reactions.

The alcohol-acid reaction.—1000 cc. of a mixture of acetic acid, ethyl alcohol and water, is prepared

containing known quantities of each of the ingredients, say 1 gram-molecule of acetic acid, 12.756 gram-molecules of the alcohol and a similar proportion of water. To this a few drops of hydrochloric acid are added, as the reaction is slow otherwise, especially in the cold. The mixture is maintained at a fixed temperature of 25°; from time to time small amounts are withdrawn and the free acetic acid determined by titration with alkali in the usual way. The diminution of acidity in a unit of time measures the speed of ether-formation, the data being expressed in gram-molecules per 1000 cc.

Time in minutes	Proportion of ether in grm. mol's	$\frac{DC_{\text{ether}}^1}{Dt}$
0	0	0
44	0 1327	0 00302
53	0 1628	0 00307
62	0 1847	0 00298
70	0.2128	0 00304
Average...		0 00303

According to reaction (2), p. 127

$$v = \frac{DC_{\text{ether}}}{Dt} = kC_{\text{acid}} C_{\text{alcohol}} = 0.00303$$

$$\text{from which } k = \frac{0.00303}{1 \times 12.756} = 0.000238$$

¹Speed of reaction at the beginning of the experiment, which diminishes with the fall in molecular concentration of the acid and alcohol.

The Water-ether Reaction.—1 gram-molecule of ethyl acetate, 12.215 gram-molecules of water and the same amount of alcohol, are mixed and allowed to stand for such a time as will permit reaching the same state of equilibrium as in the experiment with acid, water and alcohol. The mixture will have a volume of 1000 cc. and is speeded, as in the other case, with a few drops of hydrochloric acid. The experiment is carried on at 25° as before, but the *increase* of acidity is here the measure of the speed of the change, expressed in the unit of time. At the end of about 90 minutes there is found

$$v' = \frac{DC_{\text{acid}}}{Dt} = 0.001 \text{ on an average}$$

or according to reaction (2)

$$v' = \frac{DC_{\text{acid}}}{Dt} = k' C_{\text{ether}} C_{\text{water}} = 0.001$$

$$k' = \frac{0.001}{1 \times 12.215} = 0.000081$$

Equilibrium of Etherification.—To prove the law of reaction-speed that has been stated and applied, it is necessary to consider the value of k and k' as constant for different concentrations. Such determinations are lacking, but the desired proof comes indirectly from the complementary experiment made on the mixture in equilibrium.

Take, for example, the first mixture, but in place of studying its stages, allow the two reactions to

establish a condition of equilibrium, since the inverse reaction (water-ether), is feeble and does not sensibly retard the other (acid-alcohol).

It is observed that for a concentration of the ether of say, 0.7144 gram-molecule per 1000 cc., according to reaction (2)

$$\begin{aligned}C_{\text{acid}} &= 1 - 0.7144 = 0.2856 \\C_{\text{water}} &= 12.756 + 0.7144 = 13.4704 \\C_{\text{alcohol}} &= 12.756 - 0.7144 = 12.0416 \\K &= \frac{0.2856 \times 12.0416}{0.7144 \times 13.4704} = 0.352\end{aligned}$$

Now, according to the specific values of the reaction-speeds previously obtained

$$\frac{k'}{k} = \frac{0.000081}{0.000238} = 0.340$$

A value which agrees very well with the preceding. If the molecular concentrations of all the reacting substances were equal to unity, v and v' would be equal to k and k' and

$$\frac{v'}{v} = \frac{k'}{k} = 0.34$$

In other words, with equal molecules, the reaction between ethyl acetate and water is about three times less rapid than that between acetic acid and ethyl alcohol at 25°

Application to Phosphoric Chlorid.—Take the vapor of phosphoric chlorid at 182°, the temperature at which 42 per cent. of its molecules are trans-

formed (dissociated) into phosphorous chlorid and free chlorin (see p. 84).



In this state of stable equilibrium the speeds of the two opposing reactions are equal and

$$v = kC_{\text{PCl}_5} = k'C_{\text{PCl}_3}C_{\text{Cl}_2}; \quad \frac{C_{\text{PCl}_3}C_{\text{Cl}_2}}{C_{\text{PCl}_5}} = \frac{k}{k'}$$

The dissociation being accompanied by a change of volume, account must be taken of the volume occupied by the mixed gases in expressing the concentrations. Thus

$$C_{\text{PCl}_5} = C_{\text{Cl}_2} = \frac{a}{v}, \quad C_{\text{PCl}_3} = \frac{1-a}{v};$$

from which

$$\frac{a^2}{(1-a)v} = \frac{k}{k'}$$

a being the co-efficient of dissociation, = 0.42 at 182°. The volume of v is that which is occupied by the gram-molecule under consideration, increased 42 per cent. by the dissociation, and $\frac{182}{273}$ by the effect of temperature.

$$v = 1.42 \times 22.4 \left(1 + \frac{182}{273} \right) = 53 \text{ liters}$$

The expression then becomes

$$\frac{k}{k'} = \frac{(0.42)^2}{0.58 \times 53} = \frac{1}{175}$$

which can be interpreted as showing that if the concentration of each of the gases present was equal to unity, the speed of the recombination of chlorine with phosphorous chlorid would be 175 times that of the dissociation of the higher chlorid.

NON-HOMOGENEOUS EQUILIBRIUM

Examples of such systems are: A liquid in contact with its vapor, a precipitate in contact with the liquid in which it was formed, a hydrated salt and the vapor of water produced by its efflorescence, an alkali-earth carbonate and the carbon dioxide emitted by its decomposition. Whatever may be the chemical and physical characters, non-homogeneous equilibria obey the law of mass action, which is extended by recognizing the fact that no substance is absolutely insoluble or absolutely non-volatile, and that there always remains an amount, minute but constant, in the fluid and homogeneous part of the system, which is an active part, in which the equilibrium is controlled.

In support of this view, a little odd at first mention, it is simply necessary to point out that mercury, at temperatures so low that the tension of its vapor cannot be measured, is nevertheless capable of amalgamating a slip of gold foil placed near it but not in contact, for a limited time.¹

¹ Similarly, several metals are capable, at small but appreciable distances, of affecting sensitive photographic emulsions. See, Leffmann, *Jour. Frank. Inst.*, 1914, 178, 743.—Tr.

Dissociation of Calcium Carbonate.

Premising that both calcium carbonate and calcium oxid have a vapor that is constant at a given fixed temperature, then the two solids are both in excess. The equilibrium is established between CO_2 , the vapor of CaCO_3 , and that of CaO , a homogeneous system obeying the law of mass action.

$$v = k C_{\text{CO}_2} C_{\text{CaO}} \quad v' = k' C_{\text{CaCO}_3}$$

$$k' C_{\text{CO}_2} C_{\text{CaO}} = k' C_{\text{CaCO}_3}, \quad K = \frac{k'}{k} = \frac{C_{\text{CO}_2} C_{\text{CaO}}}{C_{\text{CaCO}_3}}$$

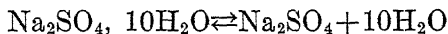
from which, C_{CaO} and C_{CaCO_3} , being constant,

$$C_{\text{CO}_2} = \text{constant}$$

Whatever may be the absolute masses of CaCO_3 and CaO that remain in the solid state, the equilibrium is such that the tension of dissociation of carbon dioxid remains constant at a given temperature. This is the law of fixed tension of dissociation, discovered by Debray, long before the law of mass action was established, of which latter it is merely an example.

Dissociation of Saline Hydrates.—The same law applies in this case. Hydrated salts lose water under the influence of heat, and even in free air at ordinary temperatures. Thus, decahydrated sodium sulfate, gives off, at 20° , vapor of water under a maximum tension of 14 mm. of mercury. The average tension of water vapor in the atmosphere is

8 to 10 mm., hence the salt effloresces in free air and becomes anhydrous, but if it is placed in a closed space with water vapor above a tension of 14 mm., it will return to the condition of decahydrate.



This is, therefore, an instance of reversible equilibrium.

The tension of the equilibrium of a salt and its vapor is measured conveniently by Bremer's tensi-

meter, shown in Fig. 27. It is a small differential manometer, in which is first placed a liquid having a very low volatility (monobromated naphthalene is suitable) which is to measure the pressure, then in the globe A, the pulverized salt, and in B, concentrated sulfuric acid to absorb the moisture. The apparatus is first placed horizontally for an instant in order that all parts may be in com-

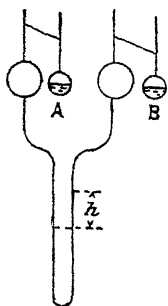


FIG. 27.

munication and an equality of pressure established at the start, then exhausted to very low pressure, sealed and placed upright. Finally it is placed in a bath of constant and known temperature until the level of the liquid is fixed. The change of level converted into millimeters of mercury is the measure of the tension of the vapor of the hydrated salt tested. This tension is fixed for a definite temperature. The result is the same as with the case of calcium carbonate, being an example of the law of mass action.

Multiple Hydrates.—Cases, similar, but more complex are noted with salts that combine with water in several proportions, that is, show several stages of hydration. One of these is copper sulfate, which may crystallize with 1, 3 or 5H₂O. Under the influence of heat, these pass directly from one to the other, each degree of hydration being in a definite equilibrium, the tension being fixed at a fixed temperature, thus

	Tension at 50° in mm. mercury.
$\text{CuSO}_4, 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4, 3\text{H}_2\text{O} + 2\text{H}_2\text{O} \dots\dots$	47 0
$\text{CuSO}_4, 3\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + 2\text{H}_2\text{O} \dots\dots\dots$	30 0
$\text{CuSO}_4, \text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + \text{H}_2\text{O} \dots\dots\dots$	4 5

If pentahydrated copper sulfate is exposed at 50°, in fine powder—to hasten the establishment of

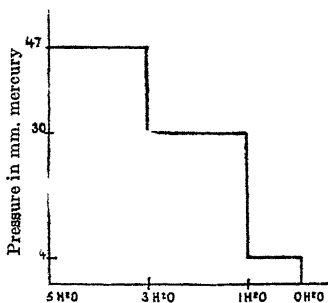
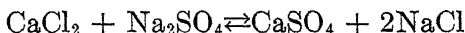


FIG. 28.

equilibrium, and the vapor of water emitted is allowed to pass off freely, the change from one system to the other will be by leaps, as will be seen in Fig. 28, which shows the change of tension as a function of the total hydration of the salt undergoing desiccation.

Equilibrium of a Precipitate with its Mother Liquor. Solubility Product.—In general, the law of mass action, exact for dilute solutions, is not strictly applicable to the case of a soluble salt in contact with its saturated solution, being generally a medium too concentrated. For precipitates, however (which are necessarily substances but little soluble), in contact with the liquid in which they are formed, the law applies, and it is possible to calculate the conditions of concentration of such an equilibrium, which condition is the typical one of analyses in the wet way.

Take the case of precipitation of calcium sulfate by the addition of a soluble sulfate to a solution of a salt of calcium.¹



1000 cc. of a saturated water-solution of calcium sulfate at 20°, contain 2.04 grm. (0.015 gram-molecule) of the salt, a concentration so low that a complete dissociation of the salt can be safely assumed. This view will give us a more detailed notion of the preceding reaction, by representing in the equation an equilibrium between the solid, its solution and the ions thereby produced.



The ions, Na and Cl, which do not change, in position or number during the precipitation, are

¹ The precipitate is usually the dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

not considered. The second equilibrium, which exists in the solution, a homogeneous medium, obeys the law

$$kC_{\text{CaSO}_4} = k'C_{\text{Ca}}^{++}C_{\text{SO}_4}^{--}$$

but C_{CaSO_4} , the molecular concentration of the small amount of un-ionized calcium sulfate, is kept constant by the excess of undissolved sulfate, and the rule of equilibrium becomes,

$$C_{\text{Ca}}^{++}C_{\text{SO}_4}^{--} = \text{constant}$$

This constant value of the product of the concentration of ions, designated, after Ostwald, the *solubility-product* controls the precipitation. Quantitatively this law is confirmed by the observations of analysts that a slight excess of reagents is required for complete precipitation. The fact is, that if to such a liquid we add, say, sodium sulfate, an increase SO_4 ions is at once produced, C_{SO_4} increases and C_{Ca} diminishes. Quantitatively, the solubility-product shows the final state of the liquid, if we know the initial concentrations and the solubility of the calcium sulfate. Thus, mix two solutions of equal volume, the one containing 0.1 grm.-mol. of sodium sulfate, the other 0.05 grm. mol. of calcium chlorid per 1000 cc. Obviously the molecular concentration of each reagent will be reduced one-half; 0.05 for the first salt and 0.025 for the second,

$$0.05 \times 0.025 = 0.00125.$$

Now the molecular concentrations of the ions SO_4 and Ca in a saturated solution at 20° are equal to that of CaSO_4 itself, that is, 0.015, grm.-mol., as has been shown above, hence,

Solubility-product of calcium sulfate

$$0.015 \times 0.015 = 0.000225,$$

a constant value at 20° . There will be precipitation until the product 0.00125 of the initial molecular concentrations of the reagents is reduced to 0.000225. Calling x the molecular proportion that has passed into the precipitate (equal for both SO_4 and Ca , which react with an equal number of molecules, we will have

$$(0.05 - x)(0.025 - x) = 0.000225$$

From this it is seen that only one value of x is possible, $x = 0.018$. There remains, finally, in the liquid in a dissociated and not precipitated state, 0.032 grm.-mol. of Na_2SO_4 and 0.007 grm.-mol. of CaCl_2 . It has been generally assumed that the precipitate is not affected by the excess of reagents and that its solubility is not affected by them, but this is generally incorrect, and is the reason that the solubility-product, though interesting in analysis in the wet way from theoretic point of view, has not yet attained much influence on practical methods.

Classification of Non-homogenous Equilibria by the Phase-rule.—The influence of physical conditions on the state of the systems in non-homogeneous

equilibrium obeys a widely applicable law due to the American chemist, Wolcott Gibbs, and deduced by him from thermodynamic principles. This law, applicable to all equilibria, physical or chemical, distinguishes in a non-homogeneous system:

Independent compounds to the number of n .

Phases, physically distinct to the number of ph .

Some variable factors, that control the condition of the system in equilibrium, which are: temperature, pressure, and the quantitative composition of each of the phases.

Finally, the degree variation, v , or number of these factors which can be modified at will without altering the number of qualitative composition of the phases.

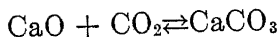
These quantities are mutually affected by the ratio,

$$\underset{\text{variation}}{v} = \underset{\text{components}}{n} + 2 - \underset{\text{phases}}{ph}$$

What is a "phase of a system"? It is a homogeneous, physical state mechanically separable, that can be distinguished from another homogeneous state of the system, without consideration of chemical composition. The dissociation of calcium carbonate presents three phases, one gaseous and two distinct solid phases, calcium oxid and undecomposed carbonate which phases are not miscible. On the contrary, in a mixture of chromium and aluminum alums, in equilibrium with a saturated solution of both there is only one liquid and one solid phase, for the two alums, though chemically

distinct, form under the conditions of the experiment, mixed crystals that are homogeneous. It is the number of distinct phases, and not the absolute mass of either that determines the conditions of equilibrium.

Of the substances that participate in a given equilibrium, the phase-rule considers only those which can vary independently of each other in this equilibrium; if any one is the result of chemical action of the others, it is not taken into account. Thus, the decomposition of calcium carbonate, brings into play only two independent components, the third, whichever it may be, being always allied to two others by the reaction



A heterogeneous system in equilibrium is defined and classed under the phase-rule, by the degree of variance. It is *invariant*, when the condition of equilibrium cannot be changed at will. Such is the case of ice, in presence of water and the vapor that this emits. The system comprises a single component and three phases,

$$v = 1 + 2 - 3 = 0$$

Ice, water and water vapor can co-exist indefinitely only at one pressure (4.6 mm. of mercury) and one temperature (0.0076°). This is also the case with the association of water and sodium sulfate, in the conditions indicated at E_2 in Fig. 17, p. 99. At this transition point, there is equilibrium between

the decahydrate, the anhydrous salt and the saturated solution of the two forms and the vapor (water and sodium sulfate) and four phases,

$$v = 2 + 2 - 4 = 0$$

E_1 , a eutectic point, shows a similar state at which co-exists ice, the decahydrate, the solution and its vapor. At the eutectic point, as at the transition

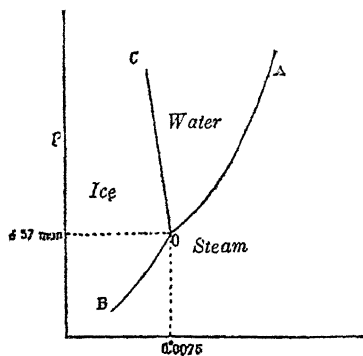


FIG. 29.

point, the fixedness of the temperature, established by experiment, is due to the invariance of the system. If, however, we attempt to modify the conditions of equilibrium of the series, ice-water-vapor, by increasing pressure above 4.6 mm. the system resists the transformation—according to a law, explained below, of displacement of equilibrium, but at the expense of the vapor, which finally disappears, after which the system will assume conditions represented by the line OC in Fig. 29.

Starting from the point O, we can act on such an invariant system by heat, without change of pressure. The system will here also react against the transformation, but in another way; the ice will disappear, absorbing the heat, and the two other phases will equilibrate according to the curve OA, which is the curve of the tension of water-vapor at different temperatures. In the two cases, the system has become monovariant

$$v = 1 + 2 - 2 = 1$$

Which indicates that we can dispose at will of one condition of equilibrium, but only one, without changing the number or qualitative composition of the phases. If we set in advance a definite pressure, that of the atmosphere, for instance, the temperature, automatically regulated by the system itself, is the zero of the ordinary thermometric scale; reciprocally a given temperature, θ , is compatible only with a certain pressure of saturated vapor, measured by $A'\theta$.

With sodium sulfate or similar salt, each portion of the curve of solubility is a point of monovariant equilibrium with two constituents, water-salt, and three phases, crystals in excess, saturated solution and vapor. Each temperature corresponds to a particular vapor-pressure, and consequently to definite concentration of the solution.

Calcium carbonate dissociating, hydrated salts efflorescing, constitute, also, monovariant systems, with two independent constituents and three phases,

one gaseous, two solid, and each temperature corresponds, as has been seen, to a definite pressure equilibrium of carbon dioxid or water.

On the contrary, the decomposition of copper oxid



although agreeing in chemical form with the two preceding cases, does not obey the law of fixed tensions at temperatures at which the mixed oxids melt, because the copper oxid will dissolve in the cuprous oxid, and forms with it a single solid phase so that there will be two independent constituents, one phase gaseous, and one solid.

$$v = 2 + 2 - 2 = 2$$

In this *bivariant* system, we can dispose at will of the two physical conditions, and a given temperature does not necessarily correspond to given pressure.

Hence the phase-rule does not inform us as what passes in the midst of a homogeneous state; it is limited to showing what are the limits of compatibility of certain states of heterogeneous equilibrium, and it is on this basis that it has served as a guide for many investigations of saturated solutions and equilibria between salts.

When it seems to fail, the fact is due to an error often easy to commit, as to the number of independent constituents, or because the system under consideration is in a condition of pseudo-equilibrium.

In other words, the transformation of the reacting substances is retarded by mechanical action.

A supersaturated solution is in pseudo-equilibrium, for it is merely necessary to introduce a minute fragment of a crystal of the dissolved substance to establish a true equilibrium. Not all substances, however, obey this rule; some are exceptional. Among these is rubidium dichromate ($\text{Rb}_2\text{Cr}_2\text{O}_7$) which exists in two forms that are capable of remaining together in saturated solution, though according to the phase rule they should co-exist only at one temperature, that of the point of transition. The salt forms two species of crystals, one monoclinic, soluble at 30° in the proportion of 9 grm. to 100 grm. of water, and the other triclinic, soluble at the same temperature in the proportion of 8.7 to 100. In spite of this difference (not very great, it is true) the two forms remain indefinitely in presence of each other under considerable variation of temperature, although, by rule, the more soluble ought to disappear to the advantage of the less soluble. Concerning this apparent exception to the phase rule it may be assumed that its operation is retarded by a passive resistance, just as friction interferes with the operations of a machine.

LAW OF DISPLACEMENT OF EQUILIBRIUM

The manner in which a system in equilibrium, homogeneous or not, reacts against disturbances to which it may be subjected is determined by a law announced first by Van't Hoff as far as concerns

temperature, and subsequently made generally applicable by Le Chatelier, as an extension of the mechanical principle that "action and reaction are equal and opposite" to the phenomena of equilibrium.

The following statement of the law is from Wm. C. McC. Lewis' *System of Physical Chemistry*, II, 109.

When a factor, determining the equilibrium of the system is altered, the system tends to change in such a way as to oppose and partially annul the alteration. That is, considering a physical or chemical system in equilibrium, this being fixed by the nature of the system and such conditions as heat and pressure, the principle states that if we alter one of these conditions, say temperature, the system will change in such direction as will tend to annul this change.

Exemplification will be limited to the two factors considered in the preceding paragraphs, the pressure, or the concentration, and the temperature.

Pressure.—Water in freezing expands; therefore, pressure causes the melting of ice, which diminishes the volume of the system and consequently, diminishes the pressure to which it is subjected.

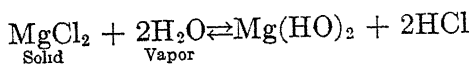
In a gaseous, homogeneous, system in which the concentration of each reacting substance is due to its partial pressure, a variation of the total pressure will or will not displace the equilibrium, according to whether the action takes place with or without change of volume. At a given temperature, the equilibrium $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ is indifferent to the

pressure, because neither of the reactions can change the volume of the system. At 448°, 21 molecules of hydrogen iodide are decomposed into hydrogen and iodine vapor, whatever may be the volume occupied by the mixture. On the contrary, the two reactions which are opposed in the equilibrium represented by the equation



being accompanied by a change of volume, an increase of pressure at a given temperature will bring about a recombination of the chlorine with the phosphorous chloride, though the temperature remains unchanged.

In these two cases, if we make a partial modification of pressure, that is, change the pressure of one constituent of the system, the equilibrium will be re-established by the partial recombination of the substance introduced. This will be the case, if to the above mixture PCl_3 and Cl_2 some chlorine is introduced, or to the mixture of H and I some hydrogen is introduced. A similar demonstration on a heterogeneous equilibrium is shown in the following equation.



An excess of water-vapor causes the fixation of the state $\text{Mg}(\text{HO})_2$, which tends to diminish the partial pressure and reciprocally, an excess of hydrogen chloride causes the reproduction of magne-

sium chlorid. The latter is about the only good method of obtaining anhydrous magnesium chlorid.

This influence of concentration on the nature of a reaction of equilibrium has been long familiar to chemists. Upon it are based some empirical rules or procedures due to Bertholet, now forgotten, which can be considered as a qualitative form of the law of mass action.

Temperature.—The example presented is that of the influence of change of temperature on the curve of solubility. When a substance dissolves with absorption of heat (*i.e.*, reducing the temperature of the mixture, which is the usual result), raising the temperature brings about an antagonistic phenomenon, namely, the solution of a further amount of the substance. The concentration of the liquid increases, and the solubility curve is ascendant. Inversely, if the substance produces heat in dissolving, as is observed with many sulfates, an increase of temperature causes a descent in the curve. It must be noted that Le Chatelier's principle, like the phase rule, is satisfactory only in application to true equilibria, and that the heat change whether positive or negative, which controls the nature of the displacement is that of solution in a liquid very nearly saturated with the given solid and not merely in water.

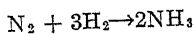
From this it follows, that if the curve of solubility of any salt, at first ascendant, reaches a maximum, and then descends, the heat change should suffer at the same time a change of sign. The correctness

of this inference has been verified in the case of calcium sulfate, of which the heat-effect of solution changes from negative to positive 30° and 40° , while the curve of solubility passes through a maximum. The same demonstration can be made with copper chlorid, $\text{CuCl}_2, 2\text{H}_2\text{O}$. This salt disengages 3.71 calories per grm.-mol. in dissolving in water, yet its solubility increases with the temperature, because the solution of it in a liquid nearly saturated (the only condition here considered) absorbs 3.2 calories per grm.-mol.¹

INFLUENCE OF TEMPERATURE ON THE SPEED OF REACTION AND THE STATE OF EQUILIBRIUM

No quantitative relation is known between reaction-speed and temperature, corresponding to that which obtains between a reaction and the concentration of the reacting substances, but it is a daily experience in the laboratory that heat brings about and speeds up many reactions. Thus, flowers of sulfur sealed in a tube with oxygen is so slightly

¹ The decomposition of ammonia, $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$, is attended by disengagement of heat and increase of volume; it is, in fact, a reversible reaction, limited in the presence of a catalyst, by a recombination,



By reason of the law that controls the displacement of equilibrium, a combination of these elements will be favored by an increase of pressure, and a decrease of temperature. (This synthesis has been applied on a large scale for some years, especially, in Germany. For an account of the theory and practice of it, see H. J. M. Creighton, *Jour. Frank. Inst.*, 1919, **187**, 399.—Tr.)

affected at ordinary temperatures that after several weeks only traces of sulfur dioxid can be detected, but at much higher temperatures, say nearly 300° , the action is so intensified that the sulfur takes fire. The same is true of carbon. At very low temperatures, chemical affinity is generally entirely suspended, but Moissan and Dewar found a striking exception in the action of fluorin and hydrogen, which combine easily at -253° .

Studies of many reactions at common temperatures seem to show that the speed of them is likely to double for each 5 or 10 degrees of increase. The relations which fail of accurate expression in the cases of the initiation of reactions are ascertainable in the cases of equilibrium, by the principles of thermodynamics.

Van't Hoff established the point, generalizing the classic formula which shows the relation between the tension of a saturating vapor and the temperature of a liquid of which the heat of vaporization is known.

$$d \text{ Log } K = - \frac{Q}{RT^2} dT$$

K is a constant of equilibrium, T the absolute temperature, R the constant of the gas, and Q the heat disengaged by the transformation of the molecular quantity in grams from the first system into the second, the volume being supposed to be constant. Assuming that Q does not vary with the temperature, true only for primary approximations,

we have by integration of the preceding equation,

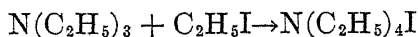
$$\text{Log } K = \frac{Q}{RT} + \text{constant}$$

and for the relation of the constants of equilibrium of the same system at two temperatures T and T'

$$\text{Log } \frac{K_2}{K_1} = \frac{Q}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

CATALYSIS

Influence of the Medium on the Speed of Reactions.—The speed of a reaction differs greatly with the nature of the solvent in which it takes place. Thus, when triethylamin unites with ethyl iodid, to form tetrethylammonium iodid



the speed of the reaction will be over seven hundred times greater if the substances are dissolved in benzyl alcohol, than if dissolved in hexane. It does not seem reasonable that differences in the viscosity of the solvent would be such as to modify the number of collisions of the molecule to such an extent as to account entirely for the difference in this reaction, yet the solvent can hardly be excluded from all participation. (There is not here a question of ionization.) This intermediate action of the solvent is allied to a class of phenomena of frequent occurrence and great practical and theoretic interest, namely, catalysis.

Catalysis.—It has been already stated that a given transformation is not necessarily possible, no more than that a body resting on an incline must necessarily roll down and lose its potential. In both cases the passage to stable equilibrium may be prevented by frictions. Substances that are capable of diminishing the interferences with combination, and causing reactions when otherwise no change would occur, or speeding up reaction otherwise slow, are called *catalysts*.¹

Catalysts do not reverse actions but facilitate them, in some such way as a lubricant promotes the action of a machine, and sometimes they give a particular direction to a reaction. They act, as pointed out in the foot-note, in very minute amount and without any quantitative ratio to the amount of change taking place. Although the list of catalysts is very large, they can in large part be classified into three groups.

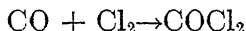
Dissolving Actions.—The most remarkable instance is that of water. Combination between hydrogen and oxygen, or hydrogen and chlorine seems to be impossible unless traces of water are present, and similar traces seem indispensable to

¹ A formal definition of a catalyst that seems to meet the present views is: "A substance that increases the velocity of a reaction without stoichiometric participation therein." The lack of quantitative relation is well illustrated by O'Sullivan's observation that one part of invertase—a catalyst existing in yeast—will convert 100,000 times its weight of sucrose into dextrose and levulose, and still be active. The term "enzym" is now largely used as a substitute for the word catalyst.—Tr.

the dissociation of ammonium chlorid, as described elsewhere. To the same type belong many *absorption* actions, such as those produced by platinum sponge, *e.g.*



and the effect of wood charcoal in forming carbon oxychlorid



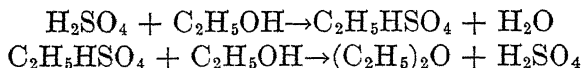
Electrolytic Contact.—Many pure metals resist the attacks of acids, but dissolve readily, when brought in contact with another metal, forming a voltaic couple. A well-known instance is that of zinc, which when very pure is scarcely acted on by dilute sulfuric acid, but if a few fragments of copper or platinum are placed in contact with it, the action begins at once.

Formation of Intermediate Compounds.—Possibly the most frequent form of catalytic action, and perhaps the only one when the action takes place in homogeneous medium, is of the type discovered by Williamson in 1850, in his memorable work on the conversion of alcohol into ether. The empirical reaction is,



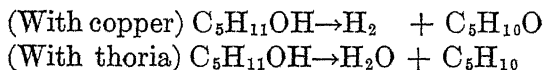
This reaction occurs only in the presence of some powerful dehydrating agent, strong sulfuric acid being the one always chosen in practice, but a small amount of the acid suffices to convert into ether a

large amount of alcohol and at the end of the operation is still present in the amount originally introduced. This fact shows that the action cannot be ascribed mainly to the dehydrating power of the acid. The essence of the action is that the acid first forms an intermediate acid, ethylsulfuric, and this is subsequently converted into ether by the action of more alcohol, by which the sulfuric acid is restored to its original condition, to again pass through the cycle.

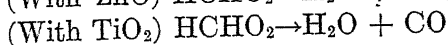
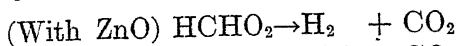


It is obvious that a small amount of the acid will suffice to form a large amount of ether.

It is rarely possible to prove the formation of the intermediate substances, but if the mechanism of catalysis is generally of this type, a catalyst is a substance which has the power to combine temporarily with one of the components of a system. In many cases, the same substance will give rise to different products when acted on by different catalysts. Thus, starch produces maltose when in contact with malt-diastrase, but a large amount of dextrose when dilute mineral acids are used. So Sabatier has shown that one of the amylic alcohols treated with copper in fine powder yields hydrogen and valeric aldehyde, but in the presence of thoria yields water and amylene



Formic acid is decomposed into hydrogen and carbon dioxide in the presence of zinc oxide, but into water and carbon monoxide in the presence of the titanous oxide



THERMOCHEMISTRY

When a substance, such as carbon, combines with oxygen actively, as seen in ordinary fires, or slowly, as occurs in vital processes, it produces a gas, carbon dioxide, which is distinguished by many properties from both its constituents and also by a less degree of latent energy equivalent to the heat produced by the combination. This heat-liberation by carbon, the basis of so large a part of industrial procedure, is regarded in thermochemistry as a measure of the affinity between carbon and oxygen, a view that is approximately correct. Carbon dioxide is capable of many reactions, not possessed by either of its constituents. It can combine with sodium oxide with heat-disengagement, and the sodium carbonate so formed will combine with water with heat-disengagement. The series of reactions has a steadily decreasing energy as measured by the heat produced, but shows that each of the compounds has a reserve of intrinsic energy, capable of being manifested through the action of some other substance, and sometimes at the expense of the molecule itself, as is the case with the modern high explosives.

The total intrinsic energy of each condition of matter is not yet known and we measure only the differences of such energies in any system of reagents, such as the combination of hydrogen with oxygen, carbon with oxygen, in relation to the final products of the combination, water or carbon dioxid. It is necessary, however, to define the two states and to know not only the chemical nature of the substances related to such energies but also the physical conditions in which the substances exist. The chemist may regard water as the same thing whether vapor or liquid, but from the thermochemical point of view, the two states differ by all the heat disengaged in passing from the former to the latter state. Similarly, a gram-molecule of hydrogen or oxygen represents energy differing with conditions of pressure and temperature, inasmuch as work is needed to compress the gas, and heat needed to raise its temperature. The forms of energy are stored in the gas and capable of being obtained from it.

Principle of Initial and Final State.—With the above reservations and when no mechanical effect is derived from the reaction itself, *the quantity* of heat disengaged or absorbed in any chemical change depends solely on the relation between the initial and final state of the system, and is the same whatever the nature and succession of the intermediate states.

As Bertholet has observed, this rule is merely the application of well-known principles of mechanics to chemical action.

Measurement of Heat of Reactions.—The principle of the methods of determining the heat produced in chemical change is simple. Known weights of the substances are combined at known temperatures and the elevation of temperature of a known weight of water observed. In practice, however, the manipulations are complicated and require much care. A simple example will show the principle of the method, the practical details not being necessary here.

300 cc. of $\frac{N}{2}$ sulfuric acid (24.5 grm. in 1000 cc.) and the same volume of $\frac{N}{2}$ potassium hydroxid (28 grm. in 1000 cc., are mixed after the temperatures are accurately noted. For calculation, it will be assumed that the temperature of the acid was 14.98° , and that of the alkali, 14.95° , and that the weight of water that is to measure the heat evolved is 3.87 grm. The specific heat of a dilute solution differs from that of pure water, by an amount within the limits of experimental error, and may be disregarded. The mean temperature of the system will be

$$\frac{(303.87 \times 14.98 + 300 \times 14.95)}{603.87} = 14.96^{\circ}$$

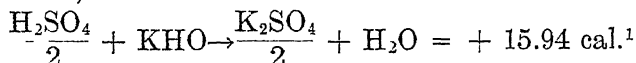
Assuming that, after all necessary corrections have been made, the temperature has risen to 18.925° , the net elevation is 3.96° and the heat-disengagement is

$$\frac{603.87 \times 3.96}{1000} = 2.391 \text{ large calories.}$$

A "large calorie" is the quantity of heat required to raise 1000 grm. of water 1°. Calculating this result to that of normal amounts of the two reagents (49 grm. of acid and 56 grm. of alkali in 1000 cc. each) we get

$$2.391 \times 2000 \div 300 = 15.94$$

that is,



In this type of experiment, an opportunity is afforded to show that the heat disengagement depends, as stated above, solely on the relation of the initial and final state of the system. By taking equal amounts of sulfuric acid and measuring the heat-disengagement due to dilution with different, known volumes of water, and then neutralizing each of these liquids in such way that the concentration of the sulfate produced shall be the same, the relative heats of combination can be determined. Experiments made long ago by Hess, using ammonium sulfate, gave the following data.

Molecules of water	Heat of dilution	Heat of neutralization	Total heat
0	0 0	16 1	16 1
1	2 1	14 0	16 1
2	3 1	12 9	16 0
5	4 2	12 0	16 2

¹ The plus sign before the figure for calories means that the reaction produces heat (exothermic). A minus sign signifies heat-absorption (endothermic). See p. 163.—Tr.

The above results are for a gram-equivalent of sulfuric acid; it will be seen that the total is sensibly the same in all cases.

Heat of Combustion.—Heats of combination with oxygen and generally with any gas, are measured under one of two conditions, constant volume and constant pressure.

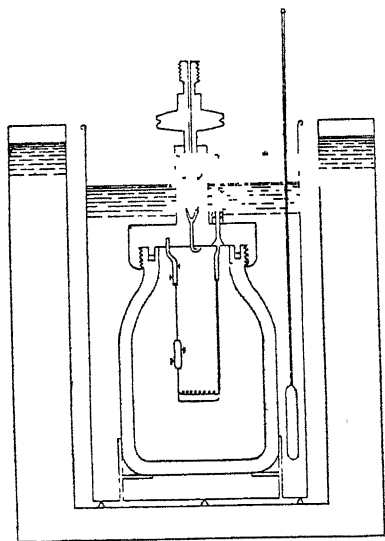
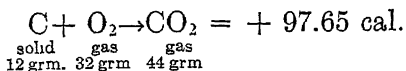


FIG. 30.

At Constant Volume.—The apparatus used is known as the bomb-calorimeter, originally devised by Berthelot, and modified by others, especially Mahler. The main features are shown in Fig. 30. In a thick-walled metallic vessel the substance to be tested is contained in small platinum boat, and the

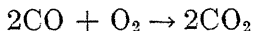
ignition started by producing incandescence in a thin iron wire. The vessel contains pure oxygen, and is immersed in water. All the weight-relations of the mass, as well as temperature must, of course, be recorded with great care. The heat of combustion of the iron wire, for example, must be deducted from the total. Pure carbon gives



The advantage of the arrangement is that it assures a complete combustion, provided the weight of the substance is such that an excess of oxygen will be present after the experiment. The method has been of wide application to organic substances, whether easily combustible or not, such as hydrocarbons, carbohydrates, proteins, and especially to food-substances. It will be shown later that the heat of formation can be deduced from the heat of combustion.

At Constant Pressure.—Whether the heat of a reaction under constant pressure will differ from that of the same reaction under constant volume, will depend on whether the volume of the system is or is not modified by the reaction. Thus, the combination of carbon with oxygen involves no change of volume, the space occupied by the carbon dioxid being the same as that occupied by the oxygen consumed, hence the heat disengagement is the same under constant pressure and constant volume. The combustion of carbon monoxid with

oxygen offers a different condition, the final volume is not the same as the original, for by the equation



it is seen that 2 volumes of carbon monoxid and 1 volume of oxygen produce only 2 volumes of carbon dioxid, that is the original volume is diminished one-third. The diminution is 11.2 liters for a gram-molecule of carbon monoxid (see p. 30). This diminution of volume corresponds to the quantity of heat equivalent to the work done at atmospheric pressure in compressing 11.2 liters of any gas.

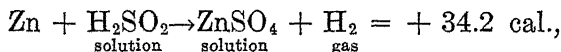
$$1.033 \times 11.2 = 11.57 \text{ kilograms.}$$

or in calories

$$11.57 \div 417 = + 0.27$$

In practice, it is more convenient to measure the heat of combustion of carbon monoxid under constant volume (68 calories for 28 grm. of CO), and add 0.27 to obtain the heat under constant pressure.

On the other hand, the solution of zinc in sulfuric acid, liberating a gas, disengages a little less heat under constant pressure than under constant volume. Thus, under constant pressure, the equation will be



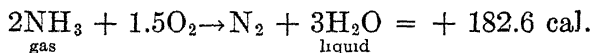
but the molecule of hydrogen in liberating itself exerts work against the atmospheric pressure, which work it takes from the reaction itself, and if we bring the relation to one of constant volume, the

equivalent of the said work in calories should be added to the preceding total, as

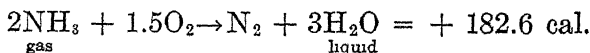
$$\frac{1.033 \times 22.4}{427} = +0.54 \text{ cal.}$$

These corrections are close to the errors of experiment, and generally of minor moment.

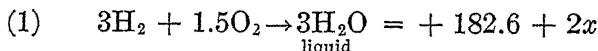
Heat of non-spontaneous Combinations.—When a combination cannot be brought about under the conditions required in the calorimeter the heat of formation can be measured by applying the principle of initial and final state. Ammonia is an instance of this method. Hydrogen and nitrogen do not combine directly, except under heat and pressure, and even then the extent of combination is small. By burning ammonia in oxygen a reversed reaction is brought about which is complete and measurable.



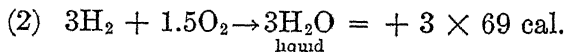
Hence, calling x the heat of formation of ammonia, we will have



which gives a total of



The heat of formation of water being known,



and from equations (1) and (2) we find

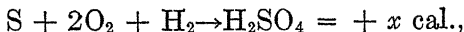
$$x = 12.2$$

and

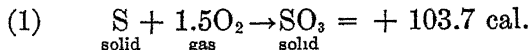


In thus suppressing the intermediate states by the addition or subtraction of the equations, we admit that the effect of the reaction is solely referable to the data of initial and final state of the system.

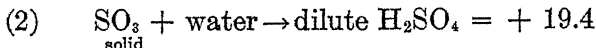
In the same general indirect manner heats of formation may be obtained for substances that cannot be synthesised in the calorimeter directly. Thus, it would scarcely be possible to secure in the calorimeter a combination of three elements such as represented in the equation,



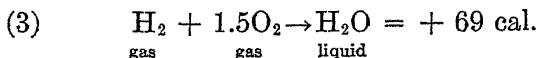
but we can proceed by two steps. In one, sulfur is burned in an excess of oxygen by catalytic action by platinum.



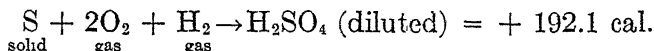
In the second step, a known weight of sulfuric anhydrid is sealed in a thin-walled glass bulb, which is broken in a mass of water of known weight and temperature. The equation is



we know further that



From (1), (2), (3) we get



Endothermic Reactions.—The chemical changes studied in the preceding paragraphs have been invariably attended by liberation of heat (exothermic) but some substances are known in the formation of which heat absorption occurs. These are termed *endothermic*. Nitrous oxid, cyanogen, acetylene and carbon disulphid are instances. To determine the heat factor in these, the procedure is the reverse of that used for exothermic substances that is, the heat of *decomposition* is measured, or a method is followed analogous to the indirect one applied in the case of non-spontaneous combinations

For instance, nitrous oxid loses its oxygen under influence of carbon monoxid, forming carbon dioxid and setting nitrogen free. The quantity of heat liberated in the reaction is greater than the quantity liberated when carbon monoxid burns directly in oxygen, which proves that some additional heat is contributed by the *exothermic decomposition* of the nitrous oxid



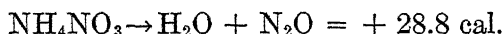
Knowing that



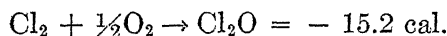
we have by subtraction



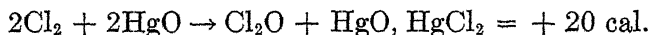
Endothermic actions are possible only when there is some exterior source of the necessary additional energy, and it is in this manner that nitrous oxid is formed under the simple decomposition by heat of ammonium nitrate. It is not the heat which is applied to the mass of nitrate, but the heat developed within the molecular structure by the combination of the hydrogen with the oxygen, a reaction that is powerfully exothermic.



Similarly, chlorin will not combine directly with oxygen to form Cl_2O , the reaction being endothermic:



but the oxid can be formed by the action of chlorin on mercuric oxid, in which the necessary heat is produced in the combination of a portion of the chlorin to form mercuric oxychlorid,



Stability of Endothermic Compounds.—Since every endothermic compound decomposes with heat-liberation, they are all essentially unstable, tending to decompose not only under mechanical disturbance, but even by heating, however, paradoxical the latter fact may appear. Cl_2O decomposes violently when heated slightly, and a curious endothermic compound of nitrogen and hydrogen, N_3H , called hydrazoic acid, is also easily decomposed by heat with violent action. Cyanogen, C_2N_2

(- 73.9 cal.) does, indeed, resist action of heat, but it is decomposed when a small amount of mercuric fulminate is exploded in contact with it.

Nevertheless some endothermic compounds, very susceptible to the action of heat, such as ozone, hydrogen peroxid, nitrous oxid, acetylene, are produced in small amount in active combustions, and in the electric arc, a phenomenon that may at first seem an example of the principle of displacement of equilibrium; bodies formed with absorption of heat, would be expected to react by their formation against the elevation of temperature, but the conditions are not those of reversible equilibrium. If, when an oxyhydrogen jet is directed against a lump of ice, hydrogen peroxid is detected in the water produced, it is because there is not an equality of temperature at every point, and the continual supply of energy, simultaneously with a great absorption of heat due to liquefaction, produces in a given time more hydrogen peroxid than is destroyed. Moreover, the heat relation may change with the temperature at which it occurs, passing from negative to positive, so that a reaction endothermic at a low temperature, may become exothermic at a high one. Acetylene is strongly endothermic, if we consider its formation from solid, polymerized carbon, as is the fact at ordinary temperatures, but in the electric arc with its large supply of intrinsic energy, the carbon is gasified, with, of course, a large addition of intrinsic energy

to it, which can be calculated, as will be seen later, and the reaction becomes exothermic.

Similarly, carbon disulfid, endothermic, when we consider it as derived from solid sulfur, becomes exothermic at 800° , the temperature at which the combination occurs, at which the sulfur is in the form of vapor and depolymerized.

Otherwise stated, and of wider application, it may be that all combinations of elements are exothermic and all decompositions endothermic and, that results in either case not conforming to this rule are due to the concurrent influence of two actions of inverse signs, or to the changes in the physical state of the elements which have the dominating part in the actions.

This view is mere surmise, and its demonstration will be difficult, but with regard to it we might suppose that nitrogen in such a compound as hydrazoic acid may be different from free nitrogen as we usually study it, and that the heat liberated by the exothermic decomposition of the compound may be due to the difference between the heat disengaged by the change of state in the element and that absorbed by the breaking of its union with hydrogen.¹

PRINCIPLE OF MAXIMUM WORK

Thermochemical data are useful in two ways. On one hand, like other physical constants, they

¹ A suggestion that nitrogen may be capable of existing in a form having much higher affinity than the common form was made many years ago by Armstrong. For a more recent investigation by Strutt, see *Jour. Chem. Soc.*, 1918, **113**, 200.—Tr.

serve to classify substances by analogy, assign a probable composition and determine the intensity of their actions, as is done with acids, with which the heat of neutralization affords a standard of activity. It is because it leads to this association with chemistry that thermochemistry has developed independently of thermodynamics, of which latter it is but a chapter, namely, that of the relation between chemical energy and heat. The other, and principle use of thermochemistry is suggest with a given system what will be the result when stability is reached. An answer to this type of question is given in close approximation, in the main exactly, by Berthelot's *law of maximum work*.

Every chemical change taking place without the introduction of energy from without, tends towards the production of a substance or a system in which the maximum amount of heat is liberated.

This principle is merely the extension of a well known principle of mechanics: all bodies submitted to the action forces tend to assume positions in which the operation of these forces is the greatest and in which the potential energy the least. By this law we can foresee the likelihood but not the absolute certainty of a reaction. Thus, sulfur burning without a catalyst, gives sulfur dioxid (69.2 cal) and not sulfuric anhydrid, which is more exothermic. This may be compared to the condition of a stone rolling in a trough which can be arrested before it reaches the lowest point. If the oxidation of sulfur is conducted in the presence of finely

divided platinum the "chemical friction" is suppressed, and sulfuric anhydrid is produced.

Experience has obliged the addition from time to time of other reservations numerous and complex, which amount practically to the view that the law of maximum work, in its original, early, form is true only of reactions taking place at rather low temperatures, in which solid substances predominate, and in which there is no disturbing influence from change of physical state or from dissociation. If, in spite of these limitations, the law is accepted by chemists, it is because the great mass of reactions take place under such conditions, or because the changes of state are compensatory between the initial and final stage of the change, as is the case with the gaeous non-metals that enter into the solid substances formulated herewith.

CaI ₂	118.6	CaO	122.0	CaBr ₂	152.0	CaCl ₂	170.0
Na ₂ O	100.0	2NaI	148.0	2NaBr	182.0	2NaCl	194.0

The figures are the calories of formation.

Since, in these cases, the system is composed of a gas and a solid, and the mean physical state remains the same, the displacement conforms exactly to the principle of maximum work; chlorin displaces bromin and bromin displaces iodine in the compounds of calcium and sodium, but oxygen displaces iodine from calcium iodide, and is displaced by it in sodium oxide.

Principle of Maximum Work and Available Energy.
—In order to utilize the principle of maximum work

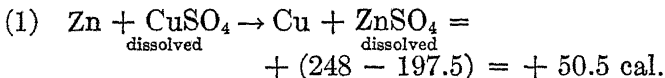
without the restrictions that have been indicated, it is sufficient to substitute in the statement the available energy in place of the total energy, a modification that thermodynamics develops. According to the second law of thermodynamics, an amount of energy that is transformed, is generally composed of two phases, one free and available, the other latent. The free energy is tantamount to the mechanical work; the latent energy is used up in the transformation.

A spontaneous transformation is invariably accompanied by a diminution of available energy, and to obtain the greatest amount of work that the system can produce, it is necessary that all changes from the initial to the final shall take place under constant temperature and in conditions not sensibly removed from a state of equilibrium; briefly, the series of changes must be isothermic and reversible. Further, when two transformations are possible, the one tends to occur which corresponds to the production of the maximum amount of available energy; the law of maximum work will, therefore, not be subject to exception if we do not confuse the available energy with the total heat disengaged in the reaction. If we knew how to make the part of the energy utilizable in a reaction as easily as we know how to measure the total heat production of it, the problem of predicting the course of any reaction would be solved, but in principle, such solution requires that the reaction should be studied in the isothermic and reversible state,

which is possible only in a limited number of cases. The most accessible are those which can be brought about in a reversible voltaic cell, equilibrated by a counter electromotive force equal to that produced in the cell itself.

ELECTROMOTIVE FORCES

Measurement of Available Energy by Electromotive Forces.—A voltaic cell is an arrangement by which the chemical energy of a reaction is transformed into electric energy, instead of being dissipated in the form of heat. Every reaction that concerns electrolytes, such as oxidation, reduction, double decomposition, displacement of metals from their salts, can be carried out on the principle of the voltaic cell. Take, for example, the last mentioned type, the displacement of copper from sulfate by zinc. It corresponds to the disengagement of a known amount of heat, equal to the difference between the heat of formation of the two sulfates.



If, instead of mixing the zinc and copper sulfate at random, we immerse the former in a solution of zinc sulfate and the latter in a solution of copper sulfate, the two solutions being separated by a porous partition, we construct what is known as Daniell's cell. It is reversible, for if we attach to the two metals, wires conducting a current of electricity in a direction opposed to that which

would proceed from the cell, then, if such current is superior in force to that of the cell, the copper will be dissolved and the zinc set free.

Now, to displace a gram-equivalent of copper requires 96494 coulombs, a quantity of electricity that will be the same for the displacement of a gram-equivalent of any element whatever, but which corresponds to a sum of electric energy different according to the tension or electromotive force under which it is delivered. Calling E this force as furnished by the cell, this sum of energy is

$$E_{\text{volts}} \times 96,494 \text{ coulombs}$$

On the other hand, the heat of displacement of one gram-equivalent of copper, expressed in electric units is

$$\frac{50.5}{2} \times 4180 \text{ joules}$$

4180 being the value, in joules, of the large calorie. And if the transformation of chemical energy into electric energy is entire:

$$E \times 96,494 = \frac{50.5}{2} \times 4180; E = 1.09 \text{ volt.}$$

which is the electromotive force of the Daniell cell.

These comparisons have been made with two forms of energy, electric and chemical, in reversible conditions under which they are interchangeable.

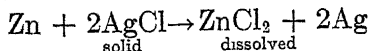
Chemical energy = gram-equivalent \times affinity

Electrical energy = quantity of electricity \times
(coulomb)
electromotive force
(volt)

These have been compared to the factors of equivalent capacities, the gram-equivalent and the coulomb, and since the respective energies are equal, by the accord of the assumed electromotive force with that found, the two factors, affinity and electromotive force can be used interchangeably. It is possible, however, that the electromotive of a reversible cell may be much smaller or much greater than the values calculated by the heat of the reaction. An instance is a cell consisting of zinc, zinc chlorid, silver chlorid and silver; the zinc being immersed in the zinc chlorid, the silver in a saturated solution of silver chlorid with an excess of the salt, the two associations being separated by a porous partition. The electromotive force of this reversible cell, slightly variable with the concentration of the zinc chlorid, is 1.015 volt, so that

$$\text{Available energy} = E \times \frac{96494}{4180} = + 23.42 \text{ cal.}$$

The reaction effected in the cell,



disengages in the same conditions of concentration +26.02 cal., so that the available energy here is 0.9 of the total energy of the reaction.

The second case is that of cell containing, zinc, potassium hydroxid, copper sulfate, copper. The electromotive force of this association is 1.4 volts instead of 1.3, calculated according to the heat of the reaction based on the gram-equivalent divided by 30,200 cal. Here the available energy exceeds

the total energy of the reaction, a result possible only by an absorption of heat from the medium in which the action takes place. This source of heat is from the solution of the products of the reaction. Hence, available energy may include not only that which is essentially chemical in source, but that due to physical phenomena, capable of furnishing, spontaneously, assistance to the electromotive force or even subtracting something from it.

SERIES OF ELECTROMOTIVE TENSIONS

It will be understood that by attacking silver chlorid, with a series of metals, such as zinc, nickel, iron and aluminum, a scale of electromotive force or affinity can be constructed in which each metal will displace those that follow, and be displaced by these that precede. The annexed table is one of such relative electromotive force: it has been constructed by an indirect method that is described in the works on electrochemistry.

Mg	1 48	H	0 00
Al	1 27	Cu''	-0 33
Mn	1 07	Hg''	-0 75
Zn	0.77	Ag	-0 77
Cd	0 42	I	-0 52
Fe''	0 34	Br	-1 0
Co	...	0 23	Cl	-1 35
Ni	0 228	SO ₄	-1 9
Pb	0 151		

This table indicates, with the order of affinities, the minimum electromotive force necessary to apply to an electrolyte to decompose it into its ions. Thus zinc chlorid requires $0.77 + 1.35 = 2.12$ volts; cop-

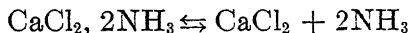
per sulfate requires $-0.33 + 1.9 = 1.57$ volts. These data have, however, strict value only for the concentration conventionally adopted, that is, a gram-equivalent per liter, for we can create an electromotive force without any chemical reaction, by immersing two portions of a metal into a solution of one of its salts, provided the concentrations are not the same around both. The electric energy obtained in such a case is derived from the spontaneous diffusion of the ions displacing themselves in the liquid and re-establishing the uniformity of concentration. This work is feeble, and corresponds to an electromotive force of a few hundredths of a volt for a difference of concentration of 1 to 10, hence the preceding order remains qualitatively identical for very different concentrations, and coincides with the order of displacement of metals, that has been long known, and also with the heat-disengagement in the formation of oxids, the oxids being less and less stable, and the metals more and more readily reducible, in proportion as they are lower in the list. This is a natural corollary of the approximation recognized between the total heat and the available energy of many reactions.

INDICATIONS OF SOME REACTIONS THAT ARE NOT IN
ACCORD WITH THE PRINCIPLE OF
MAXIMUM WORK.

$$\text{Rule } \frac{Q}{T} = \text{constant.}$$

Consideration will now be given to a type of reactions very frequently observed with the an-

hydrous metallic chlorids, and very extensively studied, because quantitative data are rather convenient to obtain. This is combination with ammonia, NH_3 . The action which resembles in several ways, the formation of saline hydrates, occurs spontaneously at low temperatures, with heat-disengagement. The compounds are called "ammoniates," and like the saline hydrates, are easily dissociated by heat and have reactions of equilibrium, thus



The question is: At what temperature does the tension of dissociation become equal to that of the atmosphere, by which the compound is wholly broken up? None of the considerations which have yet been presented affords a means of answering this question, but the answer is furnished by the following rule. The quotient of the total heat of the reaction by the absolute temperature desired is a constant equal to 0.032.

The suggestion of this rule goes back to some experiments by a physicist Trouton, who studied the absolute temperature of the boiling point of a liquid of which the heat of vaporization was known.

If the boiling point is not changed by molecular modifications, the quotient $Q \div T$, that is, the heat of vaporization divided by the boiling point is a constant. Now, the boiling of a liquid, or more exactly, the vaporization of a solid, resembles the dissociation of an ammoniate. The two phenomena

are physically analogous and by virtue of this analogy, first applied by Sainte-Claire Deville, should obey the same laws. Hence, the rule proposed by Trouton, being extended to the dissociation of a monovariant system by Le Chatelier, and further developed by Forcrand and Matignon has taken the following general form; "In all reversible phenomena, physical or chemical, in which a gaseous molecule passes to the solid state, the heat disengaged is proportional to the boiling point." To show how the rule can be expected *a priori*, it is only necessary to set side by side the expressions of the two forms of energy, chemical and calorific.

Chemical energy = mass \times affinity

Calorific energy = entropy \times temperature

Entropy is the factor of capacity of calorific energy, a factor not directly measurable, as a quantity of electricity, but quotient $Q \div T$, of two quantities measurable in an isothermic transformation Q , being the quantity of heat accompanying the transformation and T , the absolute temperature at which it accomplished.

By analogy with Faraday's law is it not reasonable to assume that in a state of reversible equilibrium, a given and constant quantity of entropy corresponds to the production of chemical masses mutually equivalent, in the same way as a constant quantity of electricity, the coulomb, corresponds to the liberation of the gram-equivalent of any

substance whatever? This confirms the rule $Q \div T$ as applicable to showing the relation of variation of entropy to the gram-molecule instead of to the gram-equivalent.

We will return to the first point of view, the analogy of the phenomena of dissociation and vaporization. When a molecule of an ammoniate takes the solid state by simple cooling, it becomes at first liquid at -32.5° , that is 240.5° , absolute, under atmospheric pressure, disengaging a heat of liquefaction, $L = 5.73$ cal. then it solidifies, disengaging a heat of solidification, $S = 1.95$ cal., measured indirectly by the difference between the heats of solution in water of 1 gram-molecule of liquid NH_3 and 1 gram-molecule of solid NH_3 .

$$\frac{Q}{T} = \frac{L + S}{T} = \frac{7.68}{240.5} = 0.032$$

When the molecule of ammoniate takes the solid form, by combination, the sum $L + S$ is increased from the heat of combination according the principle of initial and final state

$$Q' = L + S + C$$

If we know, for a series of ammoniates, on the one part the heat of formation, and on the other, the curve of tensions of dissociation, as a function of temperature, we calculate $\frac{Q'}{T'}$, being the quotient of the heat of formation by the absolute temperature

at which the tension of gaseous ammonia equals the pressure of the atmosphere.

	Q'	T'	$\frac{Q'}{T'}$
CaCl ₂ , 2NH ₃ dissociating into CaCl ₂ and 2NH ₃	14 03	453	0.0310
CuCl ₂ , 6NH ₃ dissociating into CuCl ₂ , 4NH ₃ and 2NH ₃	11.15	363	0.0307
ZnCl ₂ , 6NH ₃ dissociating into ZnCl ₂ , 4NH ₃ and 2NH ₃	11.0	332	0.0331
2AgCl, 3NH ₃ dissociating into 2AgCl..... and 3NH ₃	11.58	341	0.0340

Q' is the large calories for 1 gram-molecule of NH₃, fixed on the dry residue of the dissociation. The mean of twenty analogous instances of which the four just given were the most concordant is

$$\frac{Q'}{T'} = \frac{L + S + C}{T'} = 0.032 = \frac{L + S}{T} = \frac{Q}{T}$$

from which can be deduced, accessorially,

$$\frac{C}{T' - T} = 0.032$$

which confirms the inference from experiment, that stability grows with the increase of heat of formation of a series of analogous compounds.

The principle established by the study of the ammoniates, chosen on account of the ease of experimenting with them, may be applied to other substances. The primary equation

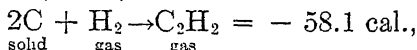
$$\frac{L + S}{T} = 0.032$$

permits us to estimate approximately the difference between the intrinsic energy of a solid and its

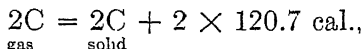
vapor at the boiling point. Assuming that carbon boils at 3500° that is, 3773° absolute, then

$$L + S = 0.032 \times 3773 = 120.7 \text{ cal.}$$

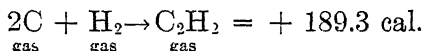
We can deduce from this that the formation of acetylene, which is endothermic, when solid carbon is the source, thus,



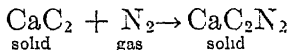
becomes powerfully exothermic at the boiling point of carbon



and the total



As an example of the application of the second ratio, $\frac{L + S + C}{T} = 0.032$, always limited to a monovariant system, we may take the reaction between nitrogen and calcium carbid. If these two will react with each other, it will be expected that the product will be calcium cyanid.



The heat of formation of calcium carbid being 13.15 cal. and that of solid calcium cyanid, 56.9 cal., the reaction, considered as reversible, will be



If this reaction could be realized it would evidently be favored by heating, but on condition of not exceeding the temperature at which the calcium cyanid will be dissociated with a tension

of nitrogen equal to the tension of the atmosphere. Now, according to the ratio $Q' \div T' = 0.032$, this limit will be

$$T = \frac{43.75}{0.032} = 1370^\circ \text{ absolute,}$$

say 1100°C .

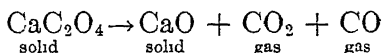
Therefore, below 100° , the fixation of nitrogen is possible, in fact, although it was long believed that no reaction would occur between nitrogen and calcium carbid, the two substances do combine about 900° , but the product is a compound of greater stability than calcium cyanid, being calcium cyanamid, CaCN_2 , now made on the large scale as a nitrogenous fertilizer.

Nernst's Formula

The ratio $\frac{Q}{T} = \text{constant}$, implies a negligible variation of the heat of reaction, Q , (except physical changes in the state of the constituents as in the case of carbon) which is less exact as the temperature is higher, the departure being greater in proportion as the dissociable substance is more stable.

	Q	$T = \frac{Q}{0.032}$	T' observed	Departure
AgCO_3	20.06	627°	498°	129
PbCO_3	22.58	706°	575°	131
MnCO_3	23.5	741°	600°	141
CaCO_3	42.5	1329°	1176°	153
SrCO_3	55.77	1743°	1428°	315

It is true that it is possible to work by successive approximations, to calculate a primary temperature T , then knowing Q and T , to calculate by the ratio (see below) the heat Q_t , corresponding to the temperature T , and deduce from the ratio $\frac{Q_t}{T} = \text{const.}$ a new value T_1 more exact than T . The rule defaults when the dissociation of the solid gives rise to two gases, as is the case with calcium oxalate.



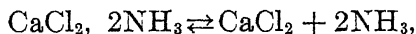
Experiment shows that it is necessary to replace the constant 0.032 by another value, 0.037.

Though much more complex, the rule given by Nernst, is preferable by reason of its general applicability:

$$(1) \log K = -\frac{Q}{4.571T} + Sn \cdot 1.75 \log T + SnC$$

This takes account at once of the number of molecules of the liberated gases and of the temperature, K being the constant of equilibrium at T ,⁰ Q the heat of the reaction under constant pressure, at ordinary temperatures, n the number of gaseous molecules, or the co-efficient of the gaseous terms of the reaction, C a constant proper to each gas and generally about 3, finally Sn and SnC , the difference between the two values of n and nC in respectively the one or other of the reactions.

In such a reaction as



there is a difference of two gaseous molecules between the first and second member of the equation,

$$S_n = 2 \quad \text{and} \quad S_n C = 6$$

The constant of equilibrium K , according to the reasoning followed apropos of the carbonates (p. 133), is

$$K = C_{NH_3}^2 C_{NH_4}$$

being the concentration, that is to say, the pressure of ammonia gas assumed to be equal to that of the atmosphere at the temperature T . From this, $K = 1$, and $\log K = 0$

$$\frac{Q}{4.571T} = 2 \times 1.75 \log T + 6$$

By replacing the second member T by 720, the absolute temperature at which the substance $\text{CaCl}_2 \cdot 2\text{NH}_3$ has a tension of dissociation equal to that of the atmospheric pressure, we find $\frac{Q}{T} = 0.073$, Q being expressed in large calories, so for a single molecule of ammonia, $\frac{Q}{T} = 0.0365$, a value very close to 0.032 given by direct experiment. On the whole, the ratio $\frac{Q}{T} = \text{constant}$, is a special case of Nernst's formula.

Volatility Rule.—Matignon has summed up qualitatively, in the following rule of volatility, the influence of the presence of the gaseous molecules,

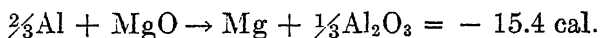
that take part in the ratio (1) (p. 181) under the terms

$$Sn1.75 \log T + SnC$$

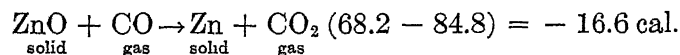
Every system of non-volatile solid or liquid substances, capable, by a new arrangement of the constituent atoms, of producing a system containing volatile substances, should exhibit such a reaction at a suitable temperature. In fact, the form

$\frac{Q}{4.571T}$, preponderating at low temperatures, diminishes as the temperature rises, and if the reaction can give rise to gaseous molecules and on the other hand, the heat of reaction, Q , is not too great, the last two terms of the equation will end by imposing their signs and $\log K$ will become positive.

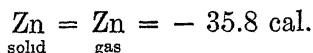
Thus, the reaction between aluminum and magnesium oxid, referred to the solid forms is endothermic



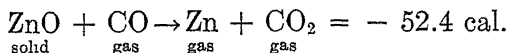
and will be more yet if we taken into account the heat of vaporization of magnesium. Nevertheless, it is a liberation of magnesium, for this is the only member of the system that is distinctly volatile at 1200°. Even if the initial system of an endothermic reaction contains gaseous molecules, the reaction is facilitated if the final state has a larger number of such molecules. This is the case with the endothermic reduction of zinc oxide by carbon monoxid



It is still more endothermic if we take into consideration the formation of zinc vapor which appears during the reaction.

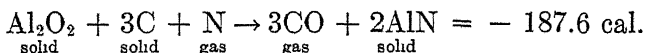


from which



In spite of the endothermic character of this reaction, carbon monoxid reduces zinc oxid readily, because there is coincidently an increase in the number of gaseous molecules.

The same condition occurs in the formation at a high temperature of aluminum nitrid,



a reaction very endothermic, but in which the first member shows a single gaseous molecule and the second three in all.

Thus, the prediction of reactions, which after exhausting the resources of the law of maximum work, has merely marked time, can be again hoped for by application of the principles and perfection of the rules that have just been set forth.

APPENDIX A

Structure of Crystals (note to page 21).—The regular forms of crystals follow two laws, those of constancy of angles and of parameters, which bear a curious analogy to the two laws of chemical combination, definite and multiple proportion, and which may be said in both cases to have their basis in discontinuity in the structure of matter. A crystal is an assemblage of molecules, or probably, groups of molecules, placed at the interlacings of a plexus in the form of a parallelopipedon, termed the plexus of Bravais. In addition to the fundamental typical form, the plexus is symmetric, in such a manner that a modification of the primary form determines a number of derived forms, the symmetries of which agree with that of the primary.

Now, geometry informs us that the elements of symmetry in a polyhedron are limited, and that parallelopipedons, classed according to the degrees of symmetry that they exhibit, will fall into seven principal types from which all natural crystal forms are derived, as follows: cubic, quadratic, orthorhombic, rhombohedric, hexagonal, monoclinic and triclinic. The abundance of symmetric forms decreases in the order of this enumeration.

The web or net-work theory of crystal forms, like the atomic theory, is not only explanatory of experiment, but expresses a physical principle somewhat crudely represented by the statement that the surface of a crystal shows under x -rays, diffraction phenomena comparable to those which are shown when ordinary light falls on a very fine mesh or grating.

It is no longer doubted that fluid crystals exist, possessing optical properties analogous to those of solids but not exhibiting rigid geometric forms, and it may be accepted that these crystals possess symmetric relations independent of any grating or web. Further information on these questions should be sought in special works on crystallography.

APPENDIX B

(Contributed by translator)

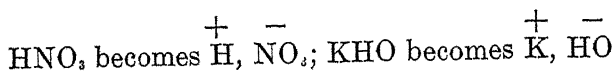
Hydrogen-ion Concentration.—As indicated in the paragraph on page 95, the acids and hydroxids differ very much as to degree of dissociation, even when compared under exactly the same conditions. So far as the well-marked members of the series are concerned, such as the stronger acids and alkalies, the degree of ionization does not affect the action of one upon the other. Thus, decinormal nitric acid (6.3 grm. in 1000 cc.) and decinormal acetic acid (6.0 grm. in 1000 cc.) are ionized in very different degrees, the former being nearly all in the form of ions, while of the latter only a small amount is dissociated, but notwithstanding this difference, if we titrate an equal volume of each with sodium hydroxid solution (the indicator and other conditions being the same), substantially the same readings will be obtained. This is because as fast as the ionized portions of the less ionized acid are used up by the alkali, other molecules of the acid become ionized to restore the ionization equilibrium, and this change takes place until all acid is neutralized.

The conditions, however, are very different when ionizable substances are in contact or reaction with a substance or surface that cannot neutralize them, as when acids or alkalies are in contact with living membranes. Here the degree of ionization affects in a great degree the activity of the substance, and it becomes important to have a method of determining the degree at any specific temperature or dilution. Water is always taken as the ionizing agent, although other liquids have some effect.

In expressing the extent of ionization of any substance, the self-ionizing action of water must be taken into account. The purest water so far obtained shows a proportion of ionization amounting to 18 grams in ten million liters. As the ionization is

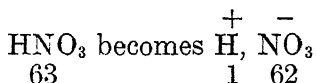


it is seen that in the purest water (which is the standard of neutrality) there is 1 gram of positively charged (acid) hydrogen, and 17 grams of negatively charged (alkaline) hydroxyl. The ionization of acids and alkalies follow the general rule.



If, therefore, the hydrogen ions in water fall below 1 grm. in ten million liters, it must be because hydroxyl ions have been introduced other than those by the self-ionization of the water, that is by some molecule containing ionizable hydroxyl. It

is possible, therefore, to indicate both acidity and alkalinity by the same notation, and this method is now pursued. Starting with a normal solution of a given acid, that is, a solution that contains 1 gram. of ionized hydrogen in a liter, the decreasing proportions, taken by tenths for simplicity, are indicated by numbers which are really the logarithms of the respective amounts of hydrogen ions, calculated in grams or fractions thereof. A general sign for the hydrogen-ion concentration has been adopted, being that suggested by Sørensen, P_H .¹ The application of the notation is best shown by an example. 63 gram. of nitric acid in 1 liter is a *normal* solution, and will contain fully ionized, 1 gram. of H-ions. In this



system the common form of logarithms is used in which the basis is 10. The logarithm of 1 on this system is zero, therefore, the hydrogen-ion concentration of a normal solution of nitric acid is indicated by P_H_0 , and all further dilutions by minus logarithms, but in the practical application of the

¹ The symbol for hydrogen ion concentration is not uniformly written by the different authorities. Leeds and Northrup (Catalog 75) use a somewhat complicated form, which is the correct one, but Clark in his recently published work on "The Determination of Hydrogen Ions," uses pH , as does also the *Jour. Biol. Chem.* It is to be hoped that a uniform symbol of simple typographic character will be adopted. That of Clark is satisfactory. The tables here given were prepared prior to the publication of Clark's book.

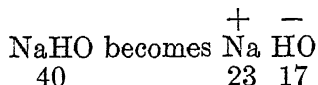
system the minus sign is omitted, so that the scheme will be as follows:

Standard	Gram-molecule of hydrogen-ion per liter	Notation	Reaction
Normal	1 0 or 10^0	P_{H_0}	acid
N 10	0 1 or 10^{-1}	P_{H_1}	acid
N 100	0 01 or 10^{-2}	P_{H_2}	acid
N 1,000	0 001 or 10^{-3}	P_{H_3}	acid
N 10,000	0.0001 or 10^{-4}	P_{H_4}	acid
N 100,000	0.00001 or 10^{-5}	P_{H_5}	acid
N 1,000,000	0 000001 or 10^{-6}	P_{H_6}	acid
N 1,000,000	0 0000001 or 10^{-7}	P_{H_7}	neutral

The last is the hydrogen-ion concentration of pure water: from this point the notation indicates alkalinity although still expressed as hydrogen-ion concentration. Attention is directed to the increase of the *hydroxyl-ion* concentration.

Gram-molecule of hydrogen ion	Gram-molecules of hydroxyl ion	Notation	Reaction
10^{-8}	0.000017	P_{H_8}	alkaline
10^{-9}	0.00017	P_{H_9}	alkaline
10^{-10}	0 0017	$P_{H_{10}}$	alkaline
10^{-11}	0 017	$P_{H_{11}}$	alkaline
10^{-12}	0.17	$P_{H_{12}}$	alkaline
10^{-13}	1.7	$P_{H_{13}}$	alkaline
10^{-14}	17.0	$P_{H_{14}}$	alkaline

The last solution is a normal alkaline solution. For example, a normal solution of sodium hydroxid is a solution of 40 gramm. of NaHO in one liter. Its ionization factors will be, if fully ionized.



that is, 17 grams of hydroxyl in a liter.

By this notation it is possible to express accurately and concisely, any degree of acidity or alkalinity. Thus, PH_5 is an acid solution; PH_9 is alkaline. For an extended and comprehensive discussion of the subject, with references to the literature, see Stroup, *Am. J. Pharm.*, 1920, **92**, 81.

INTERNATIONAL ATOMIC WEIGHTS

Jour Amer Chem Soc, 1920, 42, 1761.

Aluminum	Al	27 1	Mercury .	Hg	200 6
Antimony	Sb	120.2	Molybdenum . . .	Mo	96 0
Argon .	A	39 9	Neodymium .	Nd	144 3
Arsenic	As	74 96	Neon	Ne	20 2
Barium .	Ba	137.37	Nickel .	Ni	58 68
Bismuth .	Bi	208.0	Nitron. .	Nt	222.4
Boron	B	10 9	Nitrogen . . .	N	14 008
Bromin .	Br	79 92	Osmium .	Os	190 9
Cadmium	Cd	112 40	Oxygen	O	16 00
Cæsium	Cs	132.81	Palladium... . .	Pd	106 72
Calcium	Ca	40.07	Phosphorus .	P	31 04
Carbon	C	12 005	Platinum .	Pt	195 2
Cerium..... .	Ce	140 25	Potassium... . .	K	39 1
Chlorin.... .	Cl	35 46	Praseodymium .	Pr	140 9
Chromium .	Cr	52 0	Radium. . . .	Ra	226 0
Cobalt.. . . .	Co	58 97	Rhodium	Rh	102.9
Columbium .	Cb	93 1	Rubidium	Rb	85.45
Copper .	Cu	63.57	Ruthenium... . .	Ru	101 7
Dysprosium.....	Dy	162 5	Samarium...	Sa	150 4
Erbium	Er	167.7	Scandium	Sc	45 1
Europium .	Eu	152 0	Selenium	Se	79 2
Fluorin	F	19 0	Siheon	Si	28 3
Gadolinium .	Gd	157.3	Silver	Ag	107 88
Gallium	Ga	70.1	Sodium	Na	23 0
Germanium . . .	Ge	72.5	Strontium .	Sr	87.63
Glucium	Gl	9.1	Sulfur	S	32 06
Gold	Au	197 2	Tantalum	Ta	181 5
Helium.... .	He	4 0	Tellurium	Te	127.5
Holmium	Ho	163 5	Terbium .	Tb	159 2
Hydrogen	H	1.008	Thallium .	Tl	204 0
Indium	In	114 8	Thorium .	Th	232 15
Iodin	I	126 92	Thulium	Tm	168 5
Iridium	Ir	193.1	Tin.. . . .	Sn	118.7
Iron.... .	Fe	55 84	Tungsten	W	184.0
Krypton. . . .	Kr	82 92	Uranium .	U	238 2
Lanthanum	La	139 0	Vanadium	V	51 0
Lead.	Pb	207 20	Xenon	Xe	130 2
Lithium	Li	6.94	Ytterbium	Yb	173 5
Lutecium	Lu	175.0	Yttrium	Yt	89 33
Magnesium	Mg	24 32	Zinc	Zn	65 37
Manganese... .	Mn	54 93	Zirconium.. . .	Zr	90 6

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